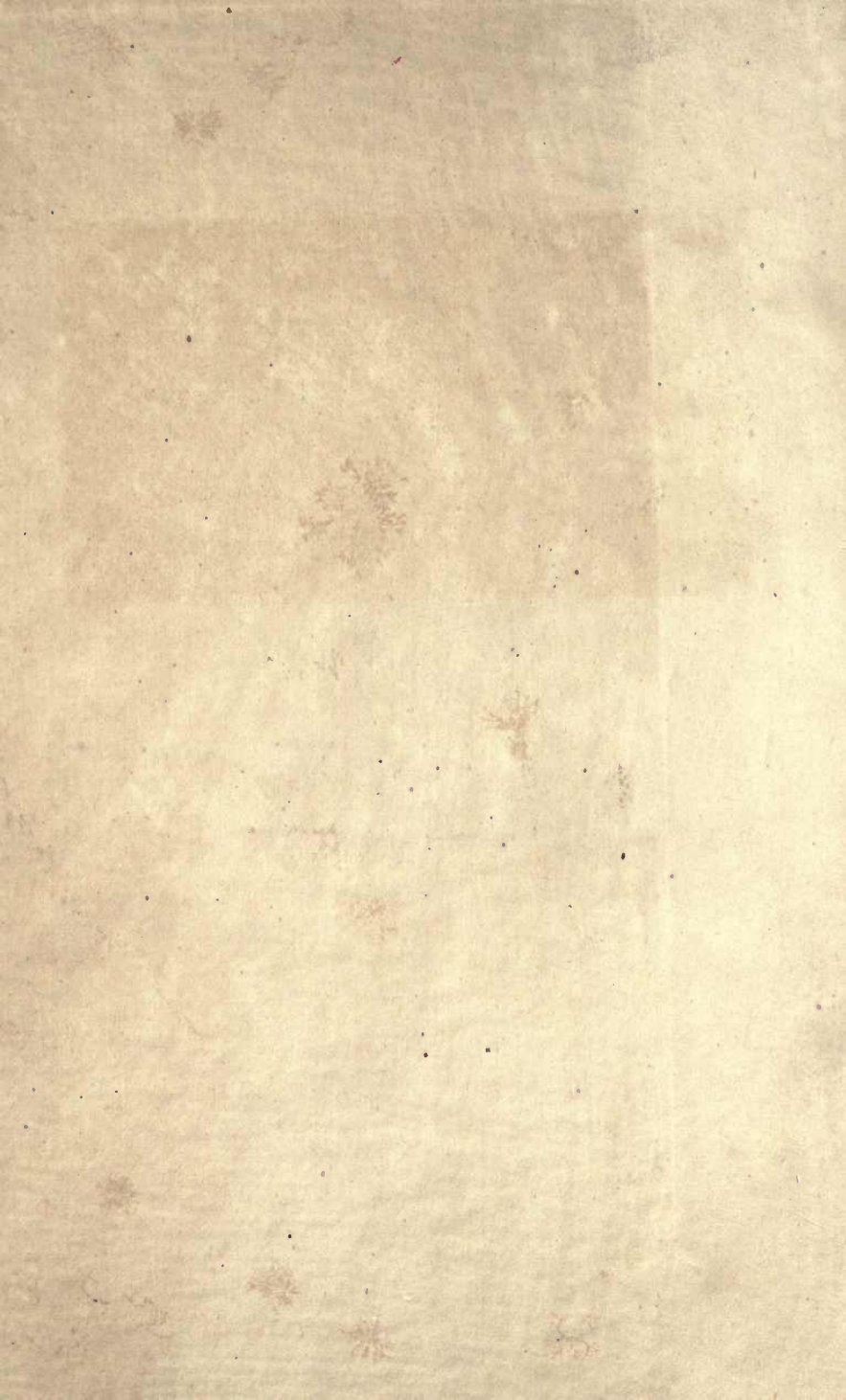
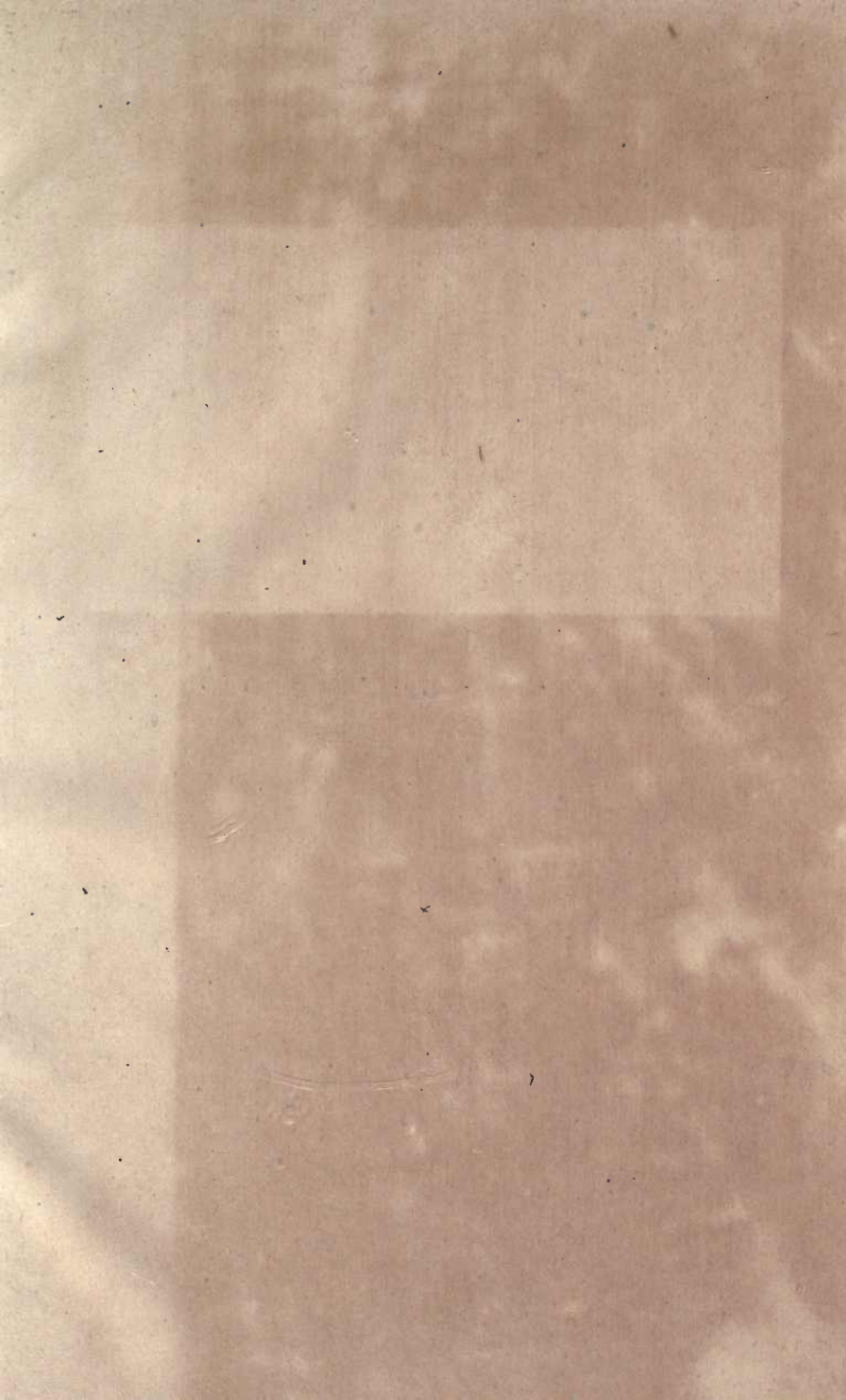


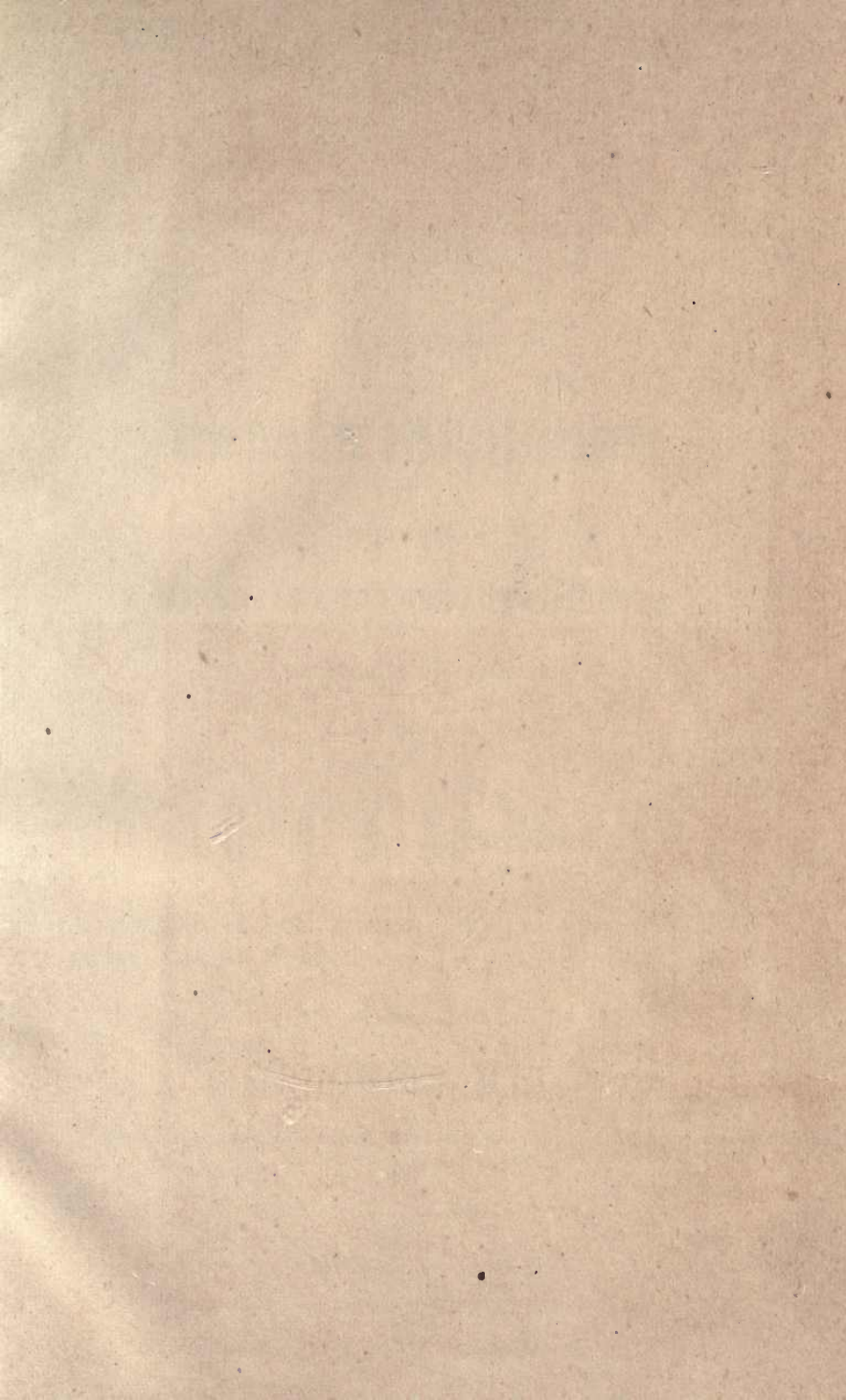
UC-NRLF

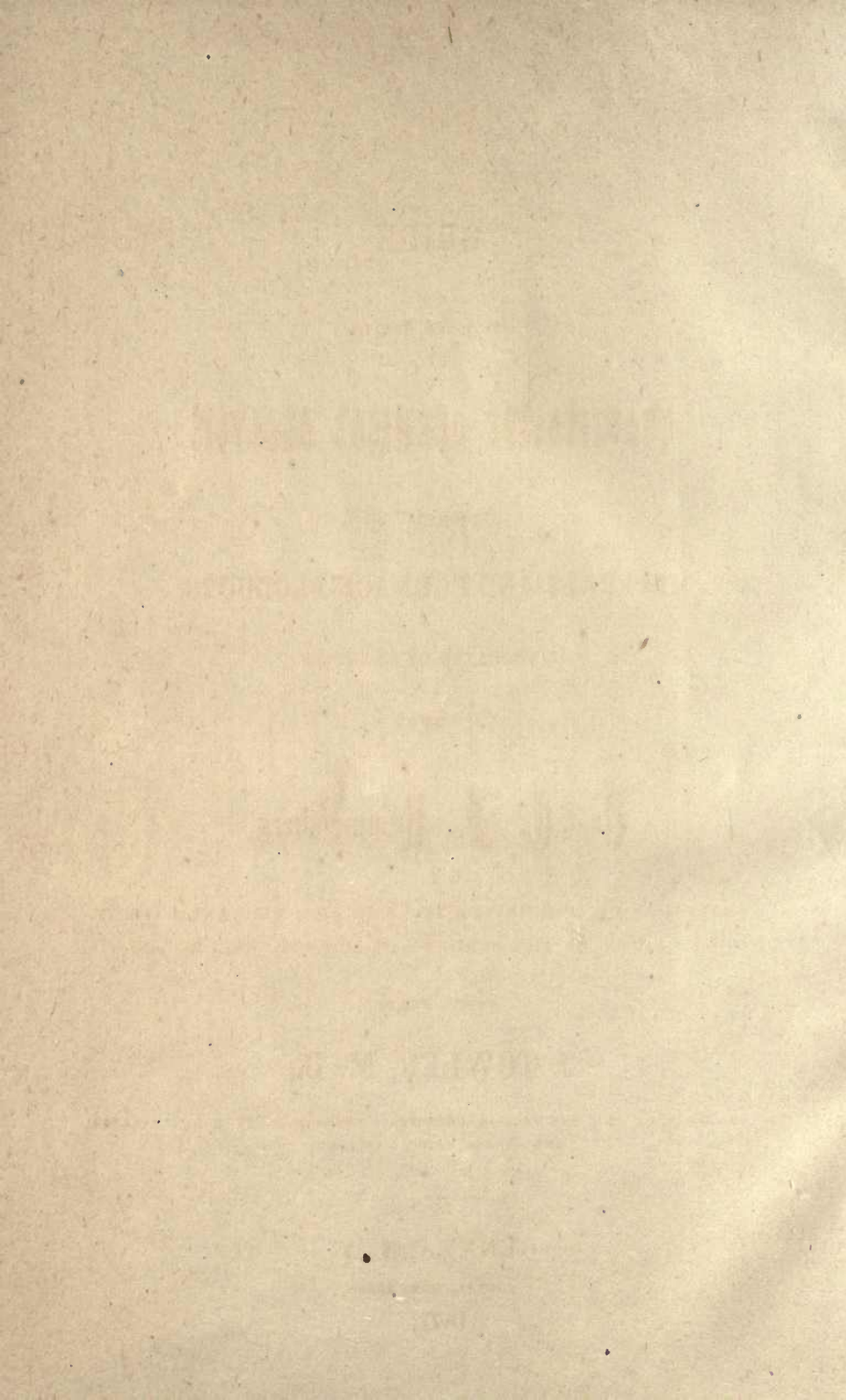


LB 620 380









GUIDE

TO A COURSE OF

QUANTITATIVE CHEMICAL ANALYSIS

especially of

MINERALS AND FURNACE-PRODUCTS,

ILLUSTRATED BY EXAMPLES,

by

Dr. C. F. Rammelsberg,

PROFESSOR AT THE UNIVERSITY AND THE MECHANICS' INSTITUTION, MEMBER OF THE ACADEMY OF SCIENCE, BERLIN, &c.

TRANSLATED BY

J. TOWLER, M. D.,

PROFESSOR OF CIVIL ENGINEERING, CHEMISTRY, TOXICOLOGY, &c, HOBART COLLEGE
AND GENEVA MEDICAL COLLEGE.

GENEVA, N. Y.

J. TOWLER, HOME PRESS.

1871.



QD 101
R32

Entered according to Act of Congress, in the year 1871, by
J. TOWLER, in the Office of the Librarian of Congress, at
WASHINGTON.

44272

TO
His Wife and Children,
WHO, BY THEIR UNTIRING PERSEVERANCE
IN
SETTING AND DISTRIBUTING TYPE,
HAVE SO ESSENTIALLY CONTRIBUTED TO ITS PUBLICATION,
THIS TRANSLATION
IS WITH AFFECTION
Inscribed
BY
THE TRANSLATOR.

TO

His Wife and Children

AND OF THEIR FURNISHING TRAVELLERS

SETTING AND DISTRIBUTING THE

NAME OF THE KNOWN DISTRIBUTION TO THE

THIS TRANSLATION

WITH ALL THE

Respected

BY

THE TRANSLATOR

PREFACE.

The following work has been translated and is now published expressly for those students in chemistry, whose time and other studies in colleges do not permit them to enter upon the more elaborate and expensive treatises of Fresenius and other authors. It is the condensed labor of a master in chemistry and of a practical analyst. In order still more to condense the translation and to diminish the expense as much as possible, the entire part on ASSAYING, as well as the chapter on the ANALYSIS of commercial drugs and metallurgical products, has been omitted; the former, because that does not properly belong to *chemical* analysis; and the latter, because the reader is generally referred to the preceding pages for a description of the analysis of the substances under consideration.

The translator has made no other changes in this work; even the old chemical equivalents have been allowed to remain unaltered, from the fact, that the results of computations in all analytical investigations are precisely the same whether the old or the new values be assigned to the different elements respectively.

The only apology, that is deemed necessary to be made in reference to the present publication, is for the want of experience and polish displayed in the typographical execution; the translator is as yet but a novice in the *black art*; but perfection is the aim of his aspirations, from which circumstance hopes may be entertained for something better in the future.

J. TOWLER.

Hobart College,
May 22, 1871.

PREFACE

The following work has been translated and is now published as a volume for those students in chemistry, whose theoretical studies in colleges do not prevent them from entering upon the more elaborate and experimental study of chemistry and other natural sciences. It is the condensed labor of a number of chemists and of a practical analyst. In order still more to condense the translation and to diminish the expense as much as possible, the entire part on Analysis, as well as the chapter on the Analysis of Commercial Drugs and Minerals, great portions have been omitted; the former, because the time and property belong to various authors; and the latter, because the reader is generally referred to the preceding pages for a description of the analysis of the substances in question.

The translator has made no other changes in this work, even the old chemical equivalents have been allowed to remain unaltered. It is the fact, that the results of numerous years in all analytical investigations are precisely the same, whether the old or the new values be assigned to the different elements respectively.

The only apology that is deemed necessary to be made in reference to the present publication is for the want of elegance and polish displayed in the English, which even now the translator is as yet but a novice in the study; but perfection is the aim of his aspirations from which no assistance hopes was to be expected by consulting for the future.

NEW YORK

Wiley & Sons
New York

CONTENTS.

	Page
I. Introduction.....	1
II. General Manipulations in Analytical Operations . . .	10
III. Vessels of Platinum and Silver.....	36
IV. Balance and Weight.....	37
V. Analysis by Measure.....	40
Analysis of separate Classes of Compounds.	
I. Metallic Alloys.....	47
A. Alloys soluble in Nitric Acid.....	49
1. Silver and Copper.....	49
2. Copper and Zinc.....	51
3. Copper, Zinc and Nickel	54
4. Lead and Zinc.....	55
5. Copper and Bismuth.....	55
6. Lead and Bismuth	56
7. Copper, Lead and Zinc.....	57
B. Alloys not completely soluble in Nitric Acid.....	57
1. Tin and Copper.....	57
2. Tin and Lead.....	59
3. Tin, Lead and Zinc.....	59
4. Tin, Copper, Lead and Zinc.....	59
5. Tin, Lead and Bismuth.....	59
6. Tin, Lead, Bismuth and Cadmium.....	60
7. Tin, Lead, Bismuth and Mercury.....	61
8. Antimony and Lead.....	60
9. Antimony and Tin.....	63
II. Metallic Oxides.....	64
1. Analysis of Iron.....	64
2. Brown Hematite, Limonite.....	65
3. Bog Iron ore.....	65
4. Magnetic Iron ore, Magnetite.....	68
5. Analysis of the Oxide of Manganese.....	69
6. Psilomelane	73
7. Oxides of Lead.....	75
8. Tin Stone, Tin Ore.....	76
III. Sulphur Metals.....	78
A. Analysis of Sulphur Metals by Aqua Regia.....	79
1. Sulphur and Iron.....	83
2. Sulphur, Copper and Iron.....	83
3. Sulphur, Copper, Iron and Zinc.....	84
4. Sulphur, Zinc, Iron and Cadmium.....	85
5. Sulphur, Antimony and Iron.....	86
B. Analysis of Metallic Sulphides by Chlorine.....	87
1. Sulphur, Antimony and Silver.....	91
2. Sulphur, Antimony and Lead.....	90
3. Sulphur, Antimony, Lead, Copper and Iron.....	92
4. Sulphur, Antimony, Arsenic, Copper, Iron and Zinc.....	92
5. Sulphur, Lead, Iron, Copper, Silver, Zinc, Nickel and Antimony	94
IV. Arsenical Metals and their Sulphides.....	95
1. Arsenic and Iron.....	95
2. Sulphur, Arsenic and Iron.....	98
3. Arsenic, Nickel, Cobalt, Iron, Copper and Antimony.....	99

VIII

	Page
4. Sulphur, Arsenic, Antimony, Nickel, Cobalt and Iron.....	103
5. Lead and Copper Mixtures.....	104
6. Arsenic and Antimony.....	106
7. Arsenic and Tin.....	107
V. Sulphates.....	108
1. Sulphate of Baryta containing Strontia.....	110
2. Sulphate of Strontia containing also Baryta and Lime.....	111
3. Alum.....	113
4. Mansfeld Black Vitriol.....	115
VI. Phosphates.....	116
1. Phosphate of Lime with Chloride and Fluoride of Calcium.....	117
2. Bone Black.....	119
3. Acid Phosphate of Lime.....	120
4. Phosphate of the oxide of Lead, Chloride of Lead with Arsenic &c.....	121
5. Phosphate of the protoxide of Iron, and Water.....	122
6. Phosphate of the protoxide of Iron, protoxide of Manganese, Lithia, &c.....	123
7. Phosphoric Acid, Alumina, oxide of Iron, Magnesia.....	126
VI. Carbonates.....	128
1. Lime, Magnesia, Carbonic Acid.....	131
2. Protoxides of Iron and Manganese, Carbonic acid, Lime and Magnesia..	134
3. Oxide of Lead, Carbonic Acid, Water.....	135
VII. Borates.....	do
1. Lime, Soda, Boracic Acid and Water.....	137
2. Magnesia, Boracic Acid, Chlorine, Water.....	138
IX. Silicates.....	do
A. Silicates decomposable by acids.....	145
1. Silicate of the oxides of Iron, sometimes with Manganese, Lime, &c....	151
2. Silicate of Alumina, Lime, Soda, Potassa and Water.....	125
3. Silicate of the protoxides of Iron and Manganese, Alumina, Lime, &c....	165
4. Silicate of the protoxide of iron, Alumina, Lime, Magnesia, Lead, &c....	158
5. Silicate of the oxide of Zinc with Water.....	159
6. Silicate of Alumina and Soda, containing Sulphide of Sodium.....	160
B. Silicates not decomposable by Acids.....	162
A. Analysis of Silicates with Carbonate of Soda.....	164
1. Silicate of Lime and Magnesia.....	170
2. Silicates of Alumina, protoxides of Iron and Manganese, Lime, &c.....	do
3. Silicate of Alumina and sesquioxide of Iron together with Water.....	do
4. Silicates containing Fluorine.....	do
5. Silicates containing Boracic Acid.....	173
B. Analysis of Silicates with Carbonate of Lime and Chloride of Ammonium.	174
C. Analysis of Silicates with Hydrofluoric Acid.....	175
1. Silicates containing no Magnesia.....	179
2. Silicates containing Magnesia.....	do
D. Decomposition of Silicates by means of Sulphuric Acid.....	181
E. Determination of the Degree of Oxidation of Iron in Undecomposable Sil:	182
F. Analysis of Mixed Silicates.....	183
1. Basalt.....	186
X. Alumina and Aluminates.....	190
1. Aluminate of Magnesia and Protoxide of Iron.....	191
2. Chrome Iron Ore.....	192
XI. Compounds of Chromium.....	do
1. Chromate of Potassa.....	do
2. Chromate of the Oxide of Lead.....	193
3. Chrome Iron Ore.....	194
XII. Compounds of Titanium.....	196
1. Titanic Iron.....	do
XIII. Compounds of Fluorine.....	198
Cryolite.....	199
XIV. Stœchiometrical Computation of the Analysis.....	do
XV. Tables for the Computation of Analyses.....	224



INTRODUCTION.

The analysis of every inorganic product, whether a mineral, some artificial compound or a product of the furnace, is two-fold: *qualitative* and *quantitative*. The qualitative analysis, which teaches how to find the constituents of the substance to be analyzed, must always precede the quantitative analysis, not alone because it is necessary to know in the first place what a body contains, before it can be thought of determining the quantity of each ingredient, but because by means of the qualitative investigation we learn what solution or decomposing material will be the most appropriate for the analysis of the body in question, a circumstance which is always dependent on the nature of its constituents. Thus the qualitative examination of a silicate, whether a mineral or a slag, tells us whether it is soluble in acids or not, the qualitative analysis of metallic sulphides can decide whether the investigation shall commence by dissolving the substance preferably in nitric acid or in aqua regia and so on.

Another advantage derived from the qualitative analysis consists in enabling the chemist at the same time to pronounce which are the principal constituents in any substance, since those ingredients, which form the largest proportion of a compound, will be the most prominent in the examination; and a moderately experienced look will soon recognize them as such. This must be kept in view in the quantitative analysis; for it is no rare occurrence that one and the same substance is separated with advantage from the rest in the compound in quite a different way, according as it exists in the combination in a larger or smaller proportion.

The quantitative analysis of inorganic bodies, as regards the

operation, is sometimes easy and sometimes more or less difficult. Even if, as is the case in the present work, which is designed for elementary instruction, the more rare substances are totally excluded, the number of metallic and non-metallic bodies which occur more frequently, is still large enough to demand various modes of separation. We shall not be able in the following pages to present *all* these single cases and illustrate them by examples, but we shall lay before our readers the *most important*, that is, those which occur most frequently.

If the different methods of quantitative modes of separation be examined more minutely, it will be found that only very few of them can lay claim to great accuracy. Among these may be reckoned, for instance, the determination of sulphuric acid by means of the salts of barium, of silver by hydrochloric acid, of lime by oxalic acid, and the reverse. In many cases a precipitate is not quite insoluble, or the presence of one body determines another to be precipitated partially by a reagent, by which, when taken alone, it is easily and completely dissolved. In this way, for example, magnesia is frequently determined by phosphate of ammonia, although the double phosphate of magnesia and ammonia is a substance somewhat more soluble in water. Alumina is slightly soluble in potassa, oxide of iron is not; but if a mixture of the two is boiled with ever so large an excess of potassa, there remains always a trace of alumina with the oxide of iron.

The first rules, therefore, to be observed by beginners in the art of chemical analysis are *accuracy* and *care*. Much depends also on skill in the mechanical operations; the operator must make himself quite at home in weighing, drying, dissolving, precipitating, filtering, evaporating &c; even the smallest loss, which might arise by spurling, pouring over the side and such like, must be avoided with the utmost care; and if such a one has occurred, the work must be immediately recommenced; for an uncertain result is worse than none at all, because, in order to arrive so far, time and labor have been sacrificed in vain. *No work must be hurried, because accura-*

cy must thereby suffer. On this account many precipitates can be filtered only a long time after the precipitation, because the latter operation is slow. Precipitates, that are to be raised to a red heat, must previously be thoroughly dried in the air, otherwise a portion may be ejected from the crucible when strongly heated. Evaporations have to be effected always by a gentle heat; for if the fluid should be raised to a boiling temperature, a portion of it would inevitably be lost by spurting.

Another very important circumstance is *the appropriate choice* of vessels in which the analytical operations have to be conducted. A principal rule to be observed in quantitative analyses is the following: *to avoid every unnecessary transference of a substance from one vessel into another*, because it is necessarily accompanied with a small loss. Every act of pouring a fluid from a beaker glass into a dish, or vice versa, diminishes the accuracy of the result; besides this, the water required to rinse out the empty vessels increases the quantity of fluid, which must frequently be diminished by evaporation; thus it would be a great fault to filter a fluid containing copper, which is to be precipitated by potassa, into a beaker, knowing that that precipitation must be effected at a boiling temperature, and that such operations can not well be performed in beaker glasses, or to do the same with a fluid, in which an alkali has to be determined by evaporation, for which purpose, as in the first case, an evaporating dish must be employed. To be desirous of effecting the solution of a metallic sulphide by means of nitro-hydrochloric acid in such a vessel, or the decomposition of a gelatinizing silicate in a retort, would be no less unsuitable, because in the former a loss might ensue in consequence of the spurting of fluid during the evolution of the gas, and in the latter case there would be considerable difficulty in general to obtain the last traces of the silicic acid deposited on the parietes of the vessel. These few remarks will be sufficient to cause beginners to exercise their minds as to the choice of proper vessels before

they undertake any analytical operation, and always to aim to make such a selection, that all subsequent operations may be performed without the necessity of rectifying the course of proceeding by a change of vessels.

The components of a substance are generally separated from one another by adding a body which produces with one of the components a combination, which, owing to its insolubility, can easily be *isolated* from the rest. Precipitates, on this account, perform an important part in chemical analysis. Nevertheless the means of *separating* a body and of its determination are not always the same. In many instances we are obliged to determine the components of a substance in a form different from that in which they exist in the substance itself, because we either can not separate the components at all as such, or at least not determine their weight in their isolated condition. *Every body must be determined in a form, in which it is least liable to change from the influence of air and heat, consequently in which its weight can be taken with the utmost accuracy.*

Thus sulphuric acid must be weighed in the form of sulphate of baryta, the protoxide of iron in the form of the sesquioxide, and copper in that of the oxide of copper. This naturally presupposes, that the constitution of the sulphate of baryta, of the sesquioxide of iron and of the oxide of copper is accurately known, which from the investigations of chemists is the case. From this consideration it becomes necessary to *make a computation*, the principles of which are laid down hereafter.

It is not however always feasible to separate a body immediately in the form in which its determination must be effected. Supposing, for example, we had a combination of sulphuric acid, oxide of copper and oxide of zinc to analyze, and know that the oxide of copper is to be determined as such. If we were, without any further consideration, to precipitate the oxide from the solution of the substance, we should commit a great error, because a part of the oxide of zinc would be thrown down at the same time, although when taken alone

the latter oxide is soluble in potassa. In this case the copper must be separated by hydrosulphuric acid from the acidified solution. The precipitate, although pure sulphide of copper, cannot again be employed for the determination of the amount of copper, because, during the act of drying and weighing, a part of the sulphide will become oxidized in the air, so that what we are weighing, represents an uncertain mixture, whose amount of copper can not be computed. The sulphide of copper, therefore, must first be converted into the oxide of copper; this latter substance may be dried and heated to a red heat without undergoing decomposition; its weight can be taken with accuracy, and its unchangeable constitution presents to us a means of determining its amount with great nicety. This example shews sufficiently, that the form, in which one substance is *separated* from another, and that, in which it is *determined*, is not always the same.

If we have to analyze an alloy of tin and lead, we shall determine the tin as oxide, and the lead in the form of sulphate, because these are the combinations in which the two metals are obtained in the most unchangeable form. In a combination of carbonic acid with the protoxide of iron, protoxide of manganese, lime and magnesia the bases are determined for similar reasons in the form of sesquioxide of iron, the double oxide and sesquioxide of manganese, the carbonate of lime and phosphate of magnesia.

Every analytical investigation must be as simple as possible; for as the number of operations increases, accuracy decreases. On this account those analyses are the most accurate in which the substance to be analyzed remains in one and the same vessel, so that it depends almost solely on the weighing how great the accuracy shall be. The analysis of those metallic oxides which are reducible by hydrosulphuric acid, as for instance of the oxides of copper, of zinc and of lead, yields therefore in proportion very accurate results; and it is such simple methods as these which chemists especially employed when their aim was to obtain the atomic weights, on which all other compu-

tations are founded. Unfortunately, however, but very few analyses can be performed in so simple a manner, most minerals and products of the furnace, having a much more complicated constitution, and thus requiring several different operations, which, notwithstanding all conscientiousness in the operator, are in proportion more prejudicial to the accuracy of the final results.

As soon as an analysis is ended, all the constituents of the body under examination determined, and from the form in which they were determined, their respective amounts in the form in which they existed in the original compound computed, it will scarcely ever happen that the sum of the separate quantities obtained will be equal to the weight of the body analyzed, or, as is customary for the sake of comparison, to compute results in the parts of 100, this number being the numerical value of the substance under examination, the sum of the constituents found will scarcely ever amount to 100. It is only now and then that such an accident may happen. On the contrary either a *loss* or an *excess* will shew itself. Such a result will take place with the work of the most experienced analyst, and it is unavoidable, since all empiric operations are more or less imperfect.

The amount of loss in an analysis is in itself no certain criterion as to the accuracy of the work; for it can not be maintained, for example, that an experienced operator ought never to exceed one per cent loss in his analysis. The judgment on the contrary is formed from the nature of the constituents to be separated and from their number. If the former are easily determined, that is, if they can be definitely separated from each other, and weighed in an unchangeable form, and if their number is only small, the loss with good work may not amount to more than that of one per cent. On the contrary a carefully performed analysis of a body, consisting of six or more constituents, and amongst these such as can not be accurately separated, the loss may amount to one, one and a half to two per cent, and yet in proportion be just as accurate

as the other where the loss was the half of one per cent. A more intimate consideration of the nature of the substances to be separated and of their number is, therefore, the only criterion as to the accuracy of the operation, and not the magnitude of the loss alone.

If, notwithstanding great care in the analysis of a substance whose constituents are few in number and such as are easily determined, a loss of several per cent is manifest at the end of the operation, this indicates a constituent not discovered in the qualitative investigation, such, for instance, as water, an alkaline compound, fluorine, ammonia &c.

It is not a rare occurrence to meet with an *excess of weight*, which is caused with beginners very generally by imperfect washing of the precipitates. Frequently it arises from the fact, that, instead of an oxide, a basic salt was thrown down, whose amount of acid was also weighed. Take the case where alumina is precipitated by ammonia, the precipitate frequently contains potassa, if the latter is present in the fluid, which is no rare occurrence. Sometimes, however, the excess in weight is only apparent, since metals, for instance, are determined and computed in the form of a higher grade of oxidation than that found in the substance examined, in which case oxygen is the cause of the excess in question; and this frequently gives the first indication of the lower grade of oxidation.

We have remarked above, that *very frequently* a body is determined in form of a combination of this selfsame body with another, and that its amount is computed from the amount of this combination according to its well known composition. This composition is not at all indifferent, and has a remarkable influence on the accuracy of the result. The smaller the quantity of the material sought in the combination with one or more other substances obtained by the analysis, the smaller will be each error in the determination, or in fine the greater the accuracy, and vice versa.

An example will illustrate this. Suppose we had to determine sulphur in a combination, and that we receive it, by

reason of the analytical method adopted, in the form of sulphate of baryta, that is, in combination with barium and oxygen, so that, in order to find its amount, we must refer to the tables to ascertain how much sulphur is contained in 100 parts of sulphate of baryta. We find that 100 parts of sulphate of baryta contain 13.73 parts of sulphur. Here then the quantity of the body to be determined is only one-tenth of the combination in which we separate and weigh it. If now we had made an error in the determination of the sulphate of baryta (and no work, even the most accurate, is absolutely accurate), and for instance had received one per cent less than we ought to have received, this error will be found, it is true, in the amount of sulphur computed therefrom, but very much diminished. If the amount of sulphate of baryta received were 0.99 instead of 1.00, the amount of sulphur by computation would be 0.1359, whilst it ought to be 0.1373. The error in the sulphate of baryta is $0.01 =$ one centigramme, whilst that in the sulphur $= 0.0014$, only about one milligramme. In other words: the error in the determination of the sulphate of baryta is diminished to about one-tenth of its absolute amount in the weight of the sulphur, or, in general terms: the error in the determination of a body in the form of a combination is diminished for this body in the ratio of the weight of the compound to that of the body itself.

If on the contrary the quantity of sesquioxide of iron in a fluid is determined by first reducing it by means of hydrosulphuric acid to the protoxide form and then computing from the amount of precipitated sulphur the quantity of sesquioxide of iron, the method is less favorable to accuracy.

For since for every atom of sesquioxide of iron ($= 80$ parts), which is reduced to the protoxide, one atom of sulphur, that is, only 16 parts are received, or the amount of the body to be computed is five times greater than that of the one from whose quantity it is determined; thus it will easily be seen, that if, for instance, we should receive 0.01 (one centigramme) of sulphur too little, the sesquioxide of iron would be compu-

ted by 0.05 (five centigrammes) too little. In such a case the error is multiplied as many times as the weight of the body found is contained in the amount corresponding to it of the body to be computed.

Can the amount of the oxygen or of the hydrogen in a combination be determined relatively with more accuracy if we separate and weigh each of these two substances in the form of water?

It sometimes happens that some one or more components in an analysis are not directly separated and determined by absolute weighing. There are substances whose accurate determination is so difficult, that it is better to determine the remaining bodies in combination with them, and to deduct their sum from the total weight of the body, in which case the difference of the quantities will represent the substance in question. In this way the quantity of water in many salts, as well as acids, such as carbonic acid, nitric acid, phosphoric acid and others, is determined from the amount of loss, but of course only when the remaining bodies can be determined with the greatest exactitude, because, as is quite evident, all errors in the determination of these components must affect the one determined indirectly.

As soon as the analysis of a body is ended, it frequently becomes important to test the separate substances qualitatively as to their purity. This is necessary, partly in order to assure one's self that the separation of the substances has been effected with sufficient accuracy, that one ingredient does not contain a portion of another and vice versa, in which case the correct sum-total of the weights of the same would not give a correct determination; partly in order to hunt for other substances in minute quantities, which may have been overlooked in the qualitative analysis, especially when but a small quantity of the given material has been employed in the investigation. These tests naturally presuppose much caution and knowledge, since it is necessary to know for each individual case what materials, during the progress of the analysis, may possibly be contained in the bodies separated. The blow-pipe on such occasions, especially with metallic substances,

will be found of great service.

If the body submitted to examination was a chemical combination, and not a mixture, the result will correspond with the laws of chemical equivalents, which present an important control as to the correctness of an analysis. It is our intention to lay before our readers in full detail in one of the last articles the method of computing stoëchiometrically the result of an analysis, and consequently we refer them to this chapter.

II. General Manipulations in Analytical Operations.

There is a certain number of operations, which recur in every or in almost every analysis, and whose execution requires a variety of little knacks, that can be learned only by practice. The most important of these will be found in what follows.

1. General Preparations. Selection. Pulverization. Elutriation. Drying.

The substance to be analyzed is not always found in pure fragments or crystals and so on, but frequently surrounded by other bodies and mixed with them, from which it has to be, if possible, with care mechanically separated, because, as will easily be comprehended, the analysis of a mixture leads to no result. Thus it is that most of the minerals occur embedded in a matrix and in company with other minerals; in slags and stones from metallurgical processes we generally find interspersed, here and there, small quantities of metals in the reguline condition, which by reason of the rapid congelation did not have time to settle. In all such cases the mechanical separation of the substance from its companions is an important circumstance; and the result is altogether dependent on its accurate execution.

It is often much more difficult than is generally supposed to liberate a substance from all adhering foreign matter in order to prepare it for an analysis; for the mineral substances occur not only in a very fine state of division in some foreign matrix, but very frequently pieces, which to all appearance are the purest, will be found, on a more minute examination, surrounded by foreign materials. We have only to take into consideration the formation of minerals by crystallization, in order to conceive, that even the well-formed crystals of a substance are not a perfect guarantee for their absolute purity. For, if a body crystallizes out of a fluid which contains other bodies also in solution, it always happens that the incipient crystals contain a trace of the mother liquor, be the latter an aqueous solution or a melted mass. The quantity of the foreign matter thus enclosed increases with the size of the crystals, so that it often happens that, in the artificial production of salts, small crystals are produced intentionally, because they are more pure (saltpetre, epsom salts, alum, &c.) If the mother liquor is colored by some foreign material, the impurity of the crystals is recognized in like manner by their color, if when pure they are white.

From this circumstance we meet in nature with substances, whose proper color is modified by some admixture: quartz in its purest varieties, as rock crystal, forming transparent crystals, is found very frequently of a yellow, red, or brown color, and owes this color to certain metallic oxides with which it is impregnated; the same thing occurs with calc-spar, heavy spar and feldspar &c.

It is evident, that it is more easy to judge as to the purity of transparent substances, than of those which are opaque. If quartz crystals were not originally transparent, we should seldom become aware of the foreign bodies, such as chlorite, rutile, specular iron ore &c, which they frequently contain. When substances are opaque we have seldom any means of testing the degree of purity of their internal parts, as long as the eye either alone or by the aid of a lens has not been able

to discover any foreign material. If larger crystals, apparently quite pure, are broken to pieces, it sometimes happens, that a small nucleus of foreign substance is found within them. Thus analcime sometimes contains a nucleus of apophyllite, zircon one of carbonate of lime, leucite a crystal of augite &c.

From all this we may deduce, that small crystals, whether colorless or slightly colored, and such as have grown on the surface and combined for the formation of druses, are the best adapted for the analyses of transparent substances, because we can more legitimately predicate as to their purity, than we could in reference to larger opaque bodies, that are at the same time colored and disseminated in a surrounding matrix; indeed sometimes compact, foliated masses, even crystals of the same substance are preferable for an analytical investigation.

But we have not always the choice; for many minerals, for instance, are found only in one state of formation. No means, therefore, must be neglected to free, as perfectly as possible, the specimen intended for analysis from all foreign matter. The composition, consequently, of many minerals is very uncertain; their formulas, notwithstanding numerous excellent analyses, are still too complicated and, therefore, doubtful, because these bodies do not occur naturally in a pure condition, and because a separation of that, which does not essentially belong to the substance, by mechanical and chemical means is impossible.

In general we are in the habit of regarding those bodies that are found in the analysis to exist only in small quantities, as unimportant, and in the summing up of the results their weights are deducted. But this is not always correct. For such bodies frequently do not constitute in themselves the impurity, but exist in chemical combination with one or more of the essential constituents. If, for instance in the analysis of a silicate consisting of lime, magnesia and protoxide of iron, a small quantity of alumina should be found, it is very improbable that this alumina should be regarded as a soli-

tary admixture; on the contrary it is much more probable that it should exist likewise as a silicate. But now the question arises, how much silicic acid belongs to the alumina, and must not also a part of the remaining bases be added in the computation? In general it is quite impossible to decide this question; and it is only when a substance is found in small quantity and belonging to one accompanying the body to be analyzed whose constitution, from other sources, is known with certainty, that we are permitted to compute the admixed quantity of the latter and to deduct it from the remaining constituents.

Suppose, for instance, we had to analyze a specimen of copper pyrites, which occurs incorporated with galena, and, after the most careful possible mechanical separation, we still find some lead together with copper, iron and sulphur, there is no doubt that this admixture of lead is to be attributed to the presence of fine particles of galena interspersed in the ore. In this case the composition of galena is known, and it can easily be computed how much sulphur is to be reckoned as belonging to the quantity of lead found.

We may pursue the same course in the analysis of geological specimens, that is to say, of mixtures of several minerals, when one of them is known. If, for instance, a doleritic stone is to be examined, consisting of a white feldspar part, and of a black augite or hornblende part, the diminutive size of the single particles often precludes the possibility of separating them mechanically. But if we know, however, from the mineralogical investigation, from its deportment with the blow-pipe &c, that the feldspar part of the compound is labradorite, or is supposed to be such with a considerable degree of certainty, the whole substance is subjected to an analysis. From the alkaline and aluminous contents we may compute the amount of labradorite in accordance with the well-known formula of this mineral, that is, we may deduct the requisite amount of silicic acid and lime; if there remains a residue, in which the silicic acid contains a quantity of oxygen double of

that contained by the remaining part of the lime and the magnesia and protoxide of iron found in the analysis, this residue is in fact augite.

We have above remarked that, when a certain material is found by the analysis to exist in minute quantity, it may often be regarded as unimportant, and on this account may be deducted. But this can not take place, if it is *isomorphous* with one of the remaining constituents, that is, when it displaces an equivalent of one of them. For instance, suppose we find in a carbonate of lime and magnesia (bitter spar, brown-spar) a small per-centage of protoxide of iron, this can not be deducted, since it is isomorphous with those bases. We may ascertain whether it must be added or not from this circumstance, namely, that it must be added only when the amount of oxygen in the bases is found to be exactly half as great as that in the carbonic acid. We must be guided, therefore, by the proportions, before we decide whether a substance is important or not.

In general it is very difficult to pronounce judgment on constituents, whose quantity is small, whether they are important or not. Comparative analyses of the material from different localities, in different forms of its occurrence, as well as regard to the nature of the substances in company with it, can alone solve the question.

After this digression we now return to the methods by which a substance to be analyzed may be separated from all foreign materials accompanying it, and then submitted to the analytical operation. In order to effect this separation the substance is folded up in a piece of paper and then broken up into small pieces, from which all the pure particles are selected carefully by means of a pair of forceps. This labor is frequently very troublesome, but it is absolutely necessary.

If metallic or magnetic iron ore is the accompanying body, it is removed with a magnet.

Sometimes the separation may happen to be of such a nature as to be capable of removal by chemical means, if the

accompanying substance, for instance, is soluble in acids, whilst the material itself is not at all affected by it. Thus many minerals may be freed from adhering calspar by pouring over the roughly pulverized mass a quantity of *dilute* hydrochloric acid and allowing it to stand some time, after which the acid portion is decanted and the substance itself is washed thoroughly clean and dried. Concentrated acids, however, must not on any account be used for this purpose, since they are almost always sure to attack the substance to be analyzed.

PULVERIZATION. — Most substances must be pulverized in order to be prepared for an analysis, so as to render them soluble or capable of separation (silicates must be fused with an alkali). At one time the powder need not be very fine, as for instance, of the carbonates, which are to be dissolved in an acid; at another it must be very fine, for example, of the silicates and metallic sulphides and arsenides. In all cases the substance is folded up in paper, broken up with a hammer into rough particles, and then comminuted in an agate mortar to a fine powder, taking care to operate with a small portion at a time in the mortar, which facilitates the comminution. The pulverizing is continued, if the powder is to be very fine, until a pinch of the material between the finger and the thumb is no longer sensitive to the touch.

Hard substances, especially if the materials are rare and all loss is to be avoided, are first pulverized in a steel mortar, and then comminuted in an agate mortar. Nevertheless by this process fine particles of steel and iron are sure to get into the powder, which may be shown by the magnet. On this account the powder must be digested in hydrochloric acid and thoroughly washed. From this it is evident, that such substances as are attacked by this acid, must not be pulverized in a steel mortar. If, however, they are so hard as to attack the agate and in this way to become impure by reason of the silicic acid in the mass, there is no alternative, the pulverization must be effected in the steel mortar; and if a very fine powder is required, it is obtained by passing the pulverized

material through a fine cambric sieve. Formerly it was customary with very hard substances to determine the increase in weight, which the powder received by being comminuted in an agate mortar; but naturally this method could not be accurate.

ELUTRIATION.—In order to obtain powder in the state of the greatest fineness, it is sometimes elutriated. This is effected by first pulverizing the substance in a mortar and then pouring water upon it in a beaker glass, stirring it up thoroughly, and, after allowing the heavier particles to settle, the turbid fluid, containing the elutriated particles, is decanted into another glass. The rough particles are again rubbed up in a mortar, again treated with water, and the operation so long repeated, until all or nearly all of the substance is fine. It is sometimes exceedingly convenient to pulverize a substance in a mortar containing a little water, from the fact that the rougher and heavier particles are thus brought continually under the pestle, and in this way the operation is hastened. The elutriated substance is allowed to settle for some time in the beaker glass, and, when the liquid is clear, decanted; after that the powder is dried at a gentle heat either in the oven or on the water bath &c.

The operation of elutriation has another advantage, which allows one to easily discern the presence of another heavier body in the last portions of the washed material, if it is one of those substances sufficiently distinguishable by their colors. Sometimes we resort especially to this plan of washing in order to separate one substance from another, which naturally is the less successful the smaller the difference of density in the two bodies.

Sometimes the wash-water is not thrown away, but is allowed to evaporate over the elutriated powder, in order not to lose the portion that may have been dissolved by the water.

FILING. FLATTENING.—In order to render alloys easily soluble, they are filed with a fine clean file, or, if malleable,

are *beaten out* into thin foil under the hammer, and then cut up into small pieces.

DRYING. — Many bodies attract moisture from the air; and this has to be removed before we proceed to the analysis. This is particularly the case with powders; and on this account they must be previously freed from all hygroscopic impurity. But in the performance of this operation we must bear in mind that some bodies contain water of crystallization, which we must not mistake for the water attracted from the atmosphere; the latter has to be removed, not the former.

Many salts contain so much water of crystallization, that the common temperature of the atmosphere is capable of removing one part, whereby they are said to effloresce. In this category may be reckoned, for instance, carbonate, sulphate and phosphate of soda and several metallic salts &c. To remove all hygroscopic moisture and whatever moisture may be enclosed between the crystalline lamellæ of such salts, artificial heat is not to be applied; but the powder is folded up in filtering paper and pressed compactly between several folds of rough blotting paper by placing it under a board loaded with a heavy weight, or between two boards capable of adjustment by means of screws. After pressure the papers are all changed and fresh ones put in their place; and the operation is repeated until the moisture is entirely removed. The powder, as soon as it is dry, is transferred at once to a covered crucible and weighed.

If the substance containing water does not effloresce, the powder is placed in a watchglass or in an open platinum crucible and then transferred to the desiccating apparatus, that is, to the bellshade standing on a board or on a plate of glass; here it is left for several hours or days over sulphuric acid. But it must be observed here, that several salts that do not effloresce in the open air, are apt to do so in the dry air of the desiccator. Such salts must be taken out before the efflorescence commences, or they must be dried afterwards as above described. It is well to weigh the substance before it

is dried, as also to place it in the desiccator and, after allowing it to remain there some time, to weigh it again.

If the water, which a substance contains, can not be removed by a temperature less than that of boiling water, the substance has to be dried either on the *water bath* or in a *drying oven*. If the former be used, the substance is placed in a covered crucible and this is fixed deeply imbedded in a dish filled with sand or shot, and then the latter is placed on the water bath; but if the drying oven is to be employed, the crucible is transferred at once to the oven and there hung up; the drying oven is then maintained at a constant temperature of 212°F . In both cases the crucible and its contents are weighed after the expiration of a short time and again placed in the oven or on the bath; and the drying is continued as long as there is any diminution of weight.

The *drying oven* is an airbath, in which substances may be exposed for any length of time to the most varied temperatures. It consists of a copper cylinder, closed at the bottom, from 3 to 4 inches high and about 3 inches in diameter; there is a lid with a narrow rim round its circumference which fits loosely on the top of the cylinder. Through an opening in this lid, near the edge, there is a thermometer fixed in a cork; and half way from the top in the inside there are three pins to support the wire triangle which is to hold the crucible. The bulb of the thermometer is protected with wire gauze, and is placed as near the crucible as possible. As soon as the substance is placed in the crucible, and the latter is covered up and fixed in position, the cylinder is heated by the flame of a lamp to the proper temperature, and the flame is so regulated as to preserve a constant thermal condition. After having been maintained at the temperature required for some time, the flame is removed, and the cylinder is allowed to cool until it can be handled with impunity; the crucible is then taken out and weighed. The operation is repeated, either at the same temperature as before, or still higher, until the consecutive weights remain the same.

It is evident, that the drying oven may be employed for substances which bear a higher temperature. A temperature between the range 248°F and 266°F is very properly applied to several bodies, although they may contain no water, but which, on account of volatile contents or such as change by heat can not be raised to a red heat, unless previously so dried, as for instance the carbonates of the earths, the oxides of the metals, protoxide of iron compounds, peroxides, &c.

Frequently a body, which contains no water chemically combined with it, may be dried in the sandbath, over the lamp at a moderate heat, or even by being raised to a red heat.

2. Analytical Operations. Dissolving. Fusing with fluxes. Digesting. Evaporating. Boiling. Precipitating. Neutralizing. Filtering. Decanting. Washing.

DISSOLVING. — The substance to be analyzed must previously be dissolved either in *water* or in an *acid*. Which of these solvents is to be used depends upon the nature of the substance, and has already been determined by the qualitative analysis. Among the acids hydrochloric acid is the most general solvent; it is employed in the concentrated condition and slightly fuming. On the contrary if a sulphur compound has to be analyzed, either concentrated *nitric acid* or *nitrohydrochloric acid* has to be employed, because hydrochloric acid either will not dissolve these compounds, or gives rise to the liberation of hydrosulphuric acid, which carries away with it a part of the sulphur. But it is found to be most convenient to produce the nitrohydrochloric acid during the course of the analysis, that is, in the first place to oxidize the substance by means of nitric acid, and then as soon as the first operation is over, and the mixture has been allowed to stand for some time, hydrochloric acid is added and the digestion is continued. In the analysis of such sulphur compounds as might easily evolve hydrosulphuric acid with nitric acid, such as sulphide of iron, sulphide of zinc and sulphide of manganese, we employ a mixture of equal parts of nitric and of hydrochloric acid, which is heated until chlorine begins to escape, and is

then poured gradually upon the substance.

Fuming nitric acid is more employed, as for instance to effect the oxidation of sulphide of lead.

Alloys require not too concentrated nitric acid, but it must be free from chlorine, especially in the presence of silver, lead and bismuth. Acid, that is too strong, dissolves such metals with great difficulty, because their nitrates are insoluble in free nitric acid.

A general rule and one, that cannot be too much impressed on beginners, is to use *no more acid in the solution of a substance than is necessary*, for an unnecessary excess is so far prejudicial to accuracy as to require afterwards for its neutralization a larger quantity of an alkali, and consequently extra washing and volatilization, and, especially if ammonia has been employed, in order to effect small losses owing to the solubility of many precipitates in ammoniacal solutions.

The solution of substances is effected in dishes, beaker glasses or flasks, and depends on the nature of those substances and of the solvents employed.

We shall not give any rules for special cases here, but shall recur to them afterwards in the description of the analytical course in individual cases, and shall limit ourselves at this stage to general remarks.

All solutions in acids, which produce an evolution of gas, must be made in glass flasks, which are heated over a spirit lamp. If a substance dissolves only very slowly, it is digested on the sand bath or in the wire net over the lamp; the flask is slightly inclined on one side, and a small funnel is placed in the neck to obviate all loss from spurting. It is very rare that a fluid is required to be raised to boiling, for this would cause a loss, as for instance in the solution of the sulphides; for, when the fluid is concentrated, there is danger of losing by volatilization some of the sulphuric acid that has been produced.

On the contrary it would not be proper to use a flask for the decomposition of the silicates by means of acids, from the

fact that silicic acid, as it separates, adheres firmly to the sides of the vessel, and can not easily be removed from a flask or retort. In such cases beaker glasses or evaporating dishes are preferable, because the contents can be digested on a sand bath until the decomposition is effected, and during the operation the vessels may be covered with a glass plate (or still preferably with a large watch glass; a glass evaporating dish or the bottom of a broken vessel).

FUSION BY FLUXES.—In analytical chemistry this operation is employed in the solution of silicates or aluminates, which are not acted upon by acids; it consists in first fusing them by the aid of the alkalis or their carbonates, the alkaline earths, or with bisulphate of potash. Most of the natural and artificial silicious compounds (slags, glasses), which contain so much silicic acid as to give a ratio of oxygen double or treble that of the bases, that is to say, most of the bisilicates and trisilicates are scarcely, if at all, acted upon by acids, and consequently can not be analyzed in this way, whilst those compounds which are less rich in silicic acid, as for instance the singulo-silicates, are decomposed by acids in such a manner, that the silicic acid separates, and the bases become soluble.

Now the former, whose number is by far the greater of the two, are fused with carbonate of soda, thus giving rise to silicate of soda, from the fact that the silicates present in the compound give up a part of their acid to the alkali, and displace the carbonic acid which passes off. The more basic compound thus produced is now in all cases easily decomposed by acids.

Bisulphate of potassa is the best flux for the aluminates and similar bodies (spinel, corundum, chrome iron); it operates only by virtue of the excess of acid, that is, as sulphuric acid alone; but sulphuric acid can not be used as a substitute, since the decomposition of those bodies requires a temperature higher than this acid can bear.

Further particulars will be found when we come to the analysis of the separate compounds.

DIGESTING consists in submitting a fluid for a long time to

a temperature below its boiling point. This operation has frequently to be resorted to in analytical chemistry in order to effect the solution or decomposition of bodies; and the same sort of vessels is used as those in effecting solutions. Furthermore, fluids are digested together with precipitates, in order that the latter may completely subside; such operations can be performed on the digester, over the lamp, or in a hot-air pipe of an ordinary stove.

EVAPORATION. — Fluids are evaporated either partially or completely (evaporation to dryness). The first takes place in order to remove volatile substances, for instance, hydrosulphuric acid from fluids from which metals have been precipitated by means of this gas, or in order to concentrate fluids in those cases where, in consequence of washing, their volume has been increased to such an extent as to render it necessary to diminish this volume for the subsequent operations. In this case it is well to evaporate the wash-waters separately, and then to add the residue to the remaining fluid. Frequently also such a solution has to be evaporated to a certain point in order to get rid of an excess of free acid, at least in a great measure, but in such cases the operation must be continued until the acids begin to volatilize, and this does not take place before most of the water has been expelled by evaporation.

The object of evaporating to dryness is to determine the amount of a non-volatile substance, as for instance, of an alkali in the form of a chloride of a metal or of a sulphate, which happens to be in the fluid, or to render certain substances insoluble, for example, silicic acid set free by acids from the silicates.

Evaporation is always effected in evaporating dishes or in crucibles; it requires much care, and particularly so, not to allow the solution to boil during the whole operation, otherwise there would be a loss by spurting. The heat, therefore, must never be allowed to rise so high as to produce this result. As soon as the work is nearly through, or if the solution contains fixed and especially gelatinous bodies, the mass

is very apt to bubble up even with a moderate temperature ; when this is the case it will be necessary to stir the substance all the while or to finish the evaporation on the water bath. The most difficulty occurs when solutions have to be evaporated to dryness in platinum, or porcelaine crucibles, because the small quantity of water is easily raised to the boiling point. This is obviated by placing the crucible on a triangle, furnished with a handle, over a lamp with a very small flame until it is properly heated, and then to withdraw the crucible from the flame and oscillate it gently so as to get the solution into a circular motion, and then promote the evaporation by blowing with the mouth ; then to bring it again over the lamp and so proceed until the mass appears dry ; the lid is now put on the crucible, and the whole is again exposed to a gentle heat. Spontaneous evaporation in a dry place is also to be recommended ; but it frequently happens in such cases, that the salts effloresce, that is, creep up to the edge of the crucible and even over to the outside, a circumstance that must be carefully guarded against.

BOILING. — The operation of boiling in quantitative analytical chemistry is to be avoided as much as possible on every occasion, because of the loss which so easily is produced by it. Nevertheless it is sometimes indispensable, and in such cases has to be performed in retorts, beaker glasses or evaporating dishes. Thus a substance from which the oxide of copper is to be precipitated by potassa, or the oxide of zinc by carbonate of soda, must be boiled with these reagents. If too the amount of oxide of iron is to be determined by metallic copper, the whole must be boiled for some time ; solutions of the protosalts of iron can be oxidized easily and completely by nitrate of potassa by boiling alone.

PRECIPITATING. — As a general rule the quantitative determination of a body is founded on the fact of its producing with another body (the precipitating reagent) an insoluble compound, from whose weight and known constitution its amount can be calculated. In this way baryta is precipitated

by sulphuric acid, lime by oxalic acid, silver by hydrochloric acid; the sulphate of baryta, the oxalate of lime and the chloride of silver being insoluble substances, so that by an adequate addition of this precipitating agent and a proper attention to all the necessary conditions every trace of baryta, lime, or silver disappears from a solution; and all that is required to be known is the weight of the resulting precipitate, in order to ascertain how much of the three ingredients was present.

But it happens just as frequently, that the precipitant separates the substance to be thrown down from its combination and takes its place. This is, for instance, always the case when an earth or a metallic oxide is precipitated by an alkali, the latter uniting with the oxide which kept those bases in solutions, and consequently separates them, since they are insoluble in aqueous and alkaline fluids.

Again it does not always happen that a body is determined in the form in which it is separated from others by means of a precipitating reagent. Thus, for instance, all metals may be precipitated completely by hydrosulphuric acid, if their solutions are in the necessary condition (acid, or alkaline, according to the nature of the metal), but not all of them can be weighed, that is, determined directly in the form of sulphides, partly because free sulphur is frequently intermingled, and partly because they are partially oxidized in drying, for example, the sulphides of iron, manganese, zinc and copper. On the contrary mercury, cadmium, antimony and arsenic can be determined as sulphides.

In order to produce a precipitation in the proper manner, it is necessary to know all the circumstances, by which it can be completely effectuated. It must be known, whether the fluid to be precipitated may be or must be acid, alkaline, or neutral, and this varies with each body. If, for instance, arsenic is to be precipitated by hydrosulphuric acid, its solution *must be acid*; if silver is to be thrown down by hydrochloric acid, the solution *may be acid*; if, on the contrary, zinc is to

be precipitated by hydrosulphuric acid, or lime by oxalic acid, its solution *must be alkaline*.

Furthermore it is not at all indifferent, whether the solution to be precipitated is in a *concentrated* or *dilute* condition. If oxide of copper is to be precipitated by potassa, the solution of the former must not be too concentrated, otherwise it will dissolve a portion of the oxide of copper. If on the contrary, oxide of iron and alumina have to be separated by potassa, the solution must be concentrated, otherwise all of the alumina will not be dissolved by the potassa.

The *temperature* of the solution to undergo precipitation is another point to be taken into consideration, from the fact that many precipitations must be made in cold solutions (that is to say, at the ordinary temperature), and for others the solutions must be warmed or even raised to the boiling temperature. Thus the oxide of copper is precipitated by potassa, and the oxides of zinc and nickel by carbonate of soda at a boiling heat.

The time, too, required to produce a complete precipitation, must not be lost sight of. Thus when solutions of lime are to be decomposed by oxalic acid, or the salts of magnesia by phosphate of ammonia, they must be set aside for at least twenty hours, before filtration is attempted, because the separation of the oxalate of lime, and that of the double phosphate of magnesia and ammonia take place gradually, and would be only imperfect, if filtration were to take place soon after the precipitants had been added.

In like manner it often happens, that a longer digestion at a gentle heat is necessary in order to produce a perfect separation of a body, it being a general rule never to filter *until the precipitate has thoroughly subsided*, and the supernatant fluid has become clear. This is necessary partly in order to test the solution by the addition of a small quantity of the precipitant, whether the precipitation is complete, and partly in order to facilitate the filtration, since many precipitates, as for instance the sulphate of baryta, easily pass through the filter when they have not thoroughly settled, and thus render

the filtrate turbid. Sometimes, too, a complete separation of the precipitate is only effected by digestion at a moderate heat, as with antimony and arsenic, when solutions of these metals have been treated with hydrosulphuric acid.

As regards the *quantity of the precipitant to be used*, it is a rule to add it in slight excess, in order to be certain that the precipitation has been completely effected. But this excess must be small, as just remarked, for an analysis will be the more accurate, the less the excess of reagents. If an acid fluid is to be precipitated by an alkali, or an alkali by an acid, the reaction itself is the surest sign when this excess is attained; for if the precipitant has a distinct odor, the manifestation of this odor indicates at once the complete precipitation, as for example, when ammonia or hydrosulphuric acid has been used. Nevertheless it is necessary here to guard against a possible deception, which arises from the fact that the space above the fluid, not the fluid itself, may give rise to this odor. It is therefore in this case, as in all cases of precipitation, indispensable to stir the mixture continually with a glass rod, to remove the vapor from the vessel by blowing with the breath, and above all things, which is always the safest plan, to add a small quantity of the precipitant after the precipitate has properly settled and the fluid has become clear.

There are cases in which practice alone can determine the right amount of the precipitant to be used. For instance in the separation of the oxide of iron and alumina it is not sufficient to add potassa just enough to produce an alkaline reaction, on the contrary an excess of it is necessary in order to produce a complete separation of the two bodies.

Finally as regards the *vessels* to be used for precipitations, it may be remarked, that when the operations have to be performed in the cold or at a moderate temperature whilst digesting, beaker glasses are most appropriate; but when the temperature of boiling water is to be applied, evaporating dishes or flasks are more suitable, although with the latter there is the difficulty of removing the last traces of the pre-

precipitate.

NEUTRALIZING. — An exact neutralization of an acid fluid by an alkali, and of an alkali by an acid is sometimes necessary and can be attained by adding gradually the neutralizing material in small quantities at a time, until litmus paper indicates the proper condition of neutralization of the fluid. In this way an acid solution of oxide of iron is neutralized with ammonia in order afterwards to be precipitated by succinate of soda. The smaller the amount of fluid, the more difficult becomes the neutralization, and the greater the attention required in the operation. If carbonic acid is contained in the fluid, the solution must be warmed in order to drive it off, for this gas has of itself an acid reaction.

FILTERING. — There is no operation in analytical chemistry that is so often repeated as that of filtration. The requisite apparatus for this purpose are funnels, filtering paper and filtering stands. The size of the filter depends entirely upon the amount of the precipitate, and not upon that of the fluid; and it is just as necessary to avoid too large as too small filters.

Good filtering paper must allow the fluids to pass quickly and clear through them, and contain the smallest amount of ashes. Quick filtering paper is especially necessary in those cases in which either the precipitate or the fluid attracts oxygen or carbonic acid from the air (filtering of sulphide of copper, sulphide of zinc and sulphide of nickel). But the absence of inorganic matter in the substance of the paper is of much more importance, when the filters have to be burned; for this remains as ashes and thus increases the weight of the precipitate. This inorganic matter consists in a great measure of sand, sulphate of lime and alumina. If the amount is small it can be determined by repeated experiments for the different sized filters and then deducted. Filtering paper, the weight of whose ashes for the ordinary sized filters amounts to more than a few milligrammes, must be rejected, since it is not possible to remove the inorganic matter from the paper

by washing with acids, &c. The so called Swedish paper does not contain less foreign material than many other sorts of filtering paper and besides this it is so thin as to allow fine precipitates to pass through its fibres. In order to prepare a filter, the first thing to be done is to select a funnel of the proper size. A piece of paper is then cut out, square in shape, and folded together so that two opposite sides come in contact. Another fold is made so that the remaining two sides overlie each other. In this way the folds all proceed from the centre to the middle of the four sides. The next thing is to fold the square into the form of a triangle, beginning at the central point again and extending to the opposite angle. Place the triangle in the funnel, central point downwards, and mark how much has to be cut off from the top; this mark must be about the one-eighth of an inch lower than the rim of the funnel. The upper part is now cut off with a pair of scissars in the form of an arc of a circle, the sides of the triangle being the radii. The filter is now opened into a quadrant and pressed against the inside of the funnel. If the inclination of the sides of the funnel is not sixty degrees, the filter will not fit; in this case it must be expanded or contracted by making a slight change in the inner folds. In every case the filter must be pressed into contact with the sides of the funnel so as to form projecting folds; the upper edge must not reach the rim of the funnel, but must be equally distant from it (a condition attained only when the filter forms a perfect circle when opened out and laid flat); and the point of the filter must be in the middle of the tube of the funnel. A filter not answering to these requirements must, in quantitative operations, be absolutely rejected. It is ready as soon as it has been once more firmly pressed into contact with the sides of the funnel and uniformly moistened with water.

Filters are also cut out by means of discs of wood or tin plate of the proper size for the funnels in general use; or for each size a quadrant of tin is cut out with turned up edges, in which the papers are laid after having been folded three

times; a similar quadrant then slides over this, and by this form the periphery of the filter is cut.

All precipitates, which do not admit of being ignited, because by this operation they would undergo some change, but which are to be dried only and in this condition weighed, require *dried and weighed filters*. In this category may be reckoned sulphur, chloride of silver, hydrofluosilicate of baryta, the double chloride of platinum and potassa, and the sulphate of the oxide of lead. A filter must never be weighed just as it is, since paper, being a hygroscopic substance, always contains a variable amount of moisture. It must, therefore, first be dried. For this purpose it is placed folded in a crucible, which is then covered with its lid and put in the drying apparatus already described, which is slowly heated to the temperature of 248°F . and kept at this temperature for at least a quarter of an hour. Numerous experiments show that a filter, which has been exposed at longest from 25 to 30 minutes to a temperature of 248° , no longer loses in weight, if it is again placed in the drying apparatus and kept a longer time at this temperature or 50°F . higher. In order to test the accuracy of the drying, all that is required is to repeat the operation; but a diminution of weight will be observed only in those cases when the drying has been too much hurried. Since in general the precipitate is afterwarde dried at the same temperature at which the filter was dried, it is only proper to fix upon a higher temperature than 212°F ., which exceedingly hastens the result. As soon as the drying apparatus has cooled down to 86° or 104°F ., the crucible is taken out and placed immediately on the balance; it is weighed accurately and afterwards the empty crucible is weighed, if its weight is not already known. The difference is the weight of the filter.

Filters, on which sulphur is to be dried, must be dried at a temperature of 212°F ., because sulphur melts at a greater temperature. But in this case the drying must be continued longer, at least half an hour, and again repeated, after the crucible has been weighed, until the weight remains constant.

It has already been remarked, that each filter must be moistened with water (alcohol) before its use. In the operation of filtering the supernatant clear fluid is first poured upon the filter, holding a glass rod on the edge of the vessel to guide the fluid upon the filter and to prevent any portion from running over the edge and outside. Should this accident take place, the vessel is placed on a glass plate, and the wet spots are afterwards cleaned off with the wash-bottle.

Care must be taken, whilst filtering, that there is no spurt- ing of the fluid; this can be avoided by directing the stream of the fluid by means of a glass rod against the sides of the filter, and by placing the end of the rod almost in apposition with the paper.

The fluid must never rise as high as the edge of the filter, in order to prevent particles of the precipitate from creeping over the edge by capillary attraction and thus reaching the glass.

As soon as the clear fluid has all been poured upon the filter, the precipitate is gently stirred up and in like manner is poured a little at a time until it is all placed upon the filter; finally the vessel is thoroughly rinsed by means of the wash-bottle and a feather, whose fibres have been cut short, or a thin piece of india-rubber tube on the end of a glass rod.

The *filtrate*, that is, the fluid that has passed through the paper, is received in a beaker glass, an evaporating dish, &c, according to the nature of the next operation; for the same instructions are valid here in reference to the right selection of vessels as before mentioned. The vessel is placed so that the inside wall is in contact with the tube of the funnel, in order that the fluid, as it passes through, may not fall freely in single drops or in a continuous stream, which might easily cause loss by spurting over.

The filter must be *covered* with a glass plate during the filtration in those cases where the contents are liable to be affected by contact with the air; as, for instance, during the filtration of metallic sulphides, which easily oxidize, or of ammo-

niacal fluids containing in solution baryta, strontia, or lime, from which, when exposed to the air, the corresponding carbonates are thrown down, and thus become mixed with the original precipitate. In all such cases the operation of filtering must be performed *as quickly as possible*, and consequently the filter must never be left empty. Furthermore the filter must also be kept covered when alcoholic solutions are filtered, as, for example, when potassa or ammonia has to be determined by chloride of platinum, owing to the volatility of those solutions. And in general, when the filtering or washing has of necessity to be postponed for some time, the same precautions must be observed, in order that the edges of the filter may not dry, a circumstance that renders it difficult to wash the filter thoroughly, as is easy to observe with colored metallic solutions.

It sometimes happens that the fluid, that has been filtered, is turbid, this takes place when the particles of the precipitates are exceedingly fine; for instance, with sulphate of baryta, the double phosphate of ammonia and magnesia, and the carbonate of protoxide of manganese; but it never occurs with viscous or gelatinous precipitates. If such an occurrence is observed, the first turbid portions are poured back into the original vessel, and the receiver is changed for another as soon as the fluid begins to run clear. Particular precautions will be recommended further on, in reference to the treatment of special substances.

DECANTING. — It is only when the supernatant fluid is perfectly clear, and when its volume is considerably larger than the consistent precipitate that has subsided beneath it, that the greater part of the fluid portion may be removed by decantation, instead of passing it through the filter. But this is seldom possible, because as a general rule some of the precipitate has become deposited on the parietes of the vessel or accumulated as a thin scum on the surface of the otherwise clear liquid beneath. The only time when it is practicable is for example, when sulphur has separated owing to the oxida-

tion of the metallic sulphide in the form of a single or several adherent specks, to remove the fluid by decanting, and subsequently, to wash off the former in several waters, and finally to rinse them in a small porcelain dish.

WASHING.—Every precipitate, collected on a filter, must be washed, lest any of the remaining substances in the fluid should be retained by it, and thus increase its weight.

Precipitates are washed either with cold or hot (boiling) water, with alcohol, or with ammoniacal solutions, according to the nature of the precipitates; and since it is intended that these bodies should gradually remove, and take place of, the original fluid, a fresh addition must never be made upon the filter before the first quantities have thoroughly drained off.

This can be effected, at least when water is used, as in most cases, by means of the wash-bottle, which at the same time stirs up the precipitate and thus brings every part of it equally into contact with the fluid. In every case it requires caution, however, not to produce any clefts in the precipitate, through which the water would quickly flow away, without penetrating the larger mass beneath.

Voluminous precipitates may be stirred up from time to time with a glass rod, taking great care not to injure the filter. The edges of the filters must be very carefully washed, for it is here that the original fluid with its contents is retained the longest.

The *amount* of wash-fluid to be poured on the precipitate each time must not be very large, because better results are obtained by small quantities oft repeated. Beginners are apt to fail very frequently in this respect, and thus soon accumulate large quantities of fluids, which the vessels cannot hold, and which have to be evaporated afterwards, all which may easily result in loss, a thing that must be avoided. But if a precipitate is difficult to wash, and on this account the amount of fluid becomes very great, the wash-water must be filtered alone, evaporated to a small and convenient volume and thus added to the filtrate to be concentrated.

The *length of time* required to wash a precipitate depends upon the nature of the latter; for many precipitates (the pulverulent and the crystalline) are easily and quickly washed, whilst others (the gelatinous) are with difficulty washed. In general the result is more quickly attained with hot water, unless there should be some particular reason why this may not be used.

The proof of a precipitate's having been thoroughly washed can be ascertained by pouring a few drops of the draining wash-water upon a smooth piece of platinum or into the platinum spoon, and then by allowing them slowly to evaporate. If there is any deposit left on the metal, the operation of washing must be renewed. But several precipitates are not always so completely insoluble as not to allow a speck to remain on the platinum, only in this case the deposit will be exceedingly small. A knowledge of the nature of different precipitates, and practice will determine what is best to be done in such cases.

3. Drying and Igniting of Precipitates. Reduction of Filtres to Ashes by Burning.

The filters, together with their properly washed precipitates, must now be set aside to dry. This can be best effected by placing the funnels, together with the filters, covered with paper, in the drying chamber of the digester on its sand bath, or in the hot-air chamber of an ordinary stove, supported on tripods or on beaker glasses without bottoms. A frame of tin standing on four legs and pierced with holes on its top, and of a size to be placed in the hot-air chamber of a stove will answer the purpose quite well, in case a digester were not at hand.

The precipitates, that have thus been dried by hot air, must now be either completely *dried* in the drying apparatus, in those cases where they rest on weighed filters, or they must be *ignited*, and in this case the filter has to be burned to ashes.

In the first case the filter together with its contents is placed

in a platinum crucible, covered loosely with its lid, and heated in the drying apparatus to the temperature at which the filter had previously alone been dried (generally 248°F.) at which temperature it is maintained uninterruptedly for half an hour at least. After the crucible has sufficiently cooled, the lid is firmly closed and transferred direct from the drying apparatus to the balance, and the operation is repeated until the weight remains constant.

But if a precipitate, on an unweighed filter, has to be ignited, the (platinum or porcelain) crucible, in which the ignition is to be performed, is placed on a sheet of smooth paper, whose edges have been cut smooth; the contents of the filter are then emptied into the crucible, and the particles of the precipitate adhering to the filter are removed as much as possible by rubbing the folds of the paper together. The filter is now folded together, first cutting off the white portions, when the precipitate is *colored*, and placed on the lid of a platinum crucible supported on a triangle; in this way it is brought over the flame of a lamp and burned. The paper is first allowed to take fire, and then the flame of the lamp is diminished as much as possible and afterwards increased again as soon as the filter has become charred. At last the platinum cover is raised to a red heat, and a piece of platinum foil half an inch wide is placed on the edge of the cover in order to institute a draft of air and thus promote the ignition of the carbon of the filter. The burned gases that arise out of the flame, carbonic acid and nitrogen, surround, so to say, the ignited substance, to which by means of the platinum as it were on a bridge, the oxygen of the atmosphere is drawn. The mass is stirred from time to time with a piece of thick platinum wire, in order that all the carbonized particles may be completely burned. As soon as there are no longer any charred particles to burn, and the cover is completely cool, the ashes are put to the rest of the precipitate and brushed off thoroughly from the lid either by means of a feather or a fine pencil. The crucible, containing the precipitate, is now

covered and gradually heated to a red heat ; it is now tilted a little on one side, the lid being pushed back so as to expose the contents, and the piece of platinum foil is again placed on the edge of the crucible, in order that whatever fibres of paper may have been abraded from the filter and now contained in the precipitate, may burn, or if, as is the case with many metallic oxides, a reduction has taken place at different points, the reduced metal must again be oxidized. After a proper amount of ignition, the temperature and continuation of which depend upon the nature of the precipitates, the crucible is closed up tight, and, *as soon as it has cooled*, it is placed in the balance and weighed. This is the more necessary from the fact, that all ignited pulverulent substances are in the highest degree hygroscopic ; and, if the crucible can not be weighed right away, in all exact experiments, it must be placed under the bell shade in a vacuum over sulphuric acid.

When filters are burned on the cover of a platinum crucible, there is always the possibility of losing some of the ashes by reason of the draft of air ; and this is particularly the case with light, flocculent precipitates, as, for example, with dried silicic acid. In such cases as soon as the greatest part of the precipitate has been poured into the crucible, it is much safer to put the filter also in, to cover it well up and then to raise the temperature gradually until the filter is carbonized.

When this has taken place the lid is shoved slightly on one side so as to open the crucible partially, and the charred paper is burned with the aid of the platinum foil laid over the edge of the crucible to institute a current of air.

The same process is followed, too, when the amount of precipitate is so small as not to be capable of being removed from the filter, the latter together with the adhering precipitate being treated entirely in the crucible.

It is frequently not easy to drive the carbon from the charred filter, especially when the temperature is raised too high, in which case the carbon is less combustible, and the access of

air is too feeble; or when the filter contains precipitates which are not quite insoluble, and are thus protected from burning from the fact that the fibres are surrounded with a film of the precipitate, as is the case with the double phosphate of ammonia and magnesia.

It has already been observed, that filtering paper must contain as little ash as possible, in order that its weight need not be taken into consideration, or that its amount may be determined beforehand for the different sized filters.

III. Vessels of Platinum and Silver.

The accuracy of analytical experiments has been greatly increased by the application of crucibles, dishes, &c, of platinum. Owing to the expense, however, of such apparatus, it becomes necessary to avoid all circumstances by means of which these vessels might be injured.

Platinum crucibles are indispensable in quantitative analyses for the drying and burning of filters, for the igniting and weighing of precipitates, for the evaporation of fluids in which alkalies are to be determined, and for the heating and igniting of residues after evaporation, finally for the fusion of silicates, aluminates, &c, by means of fluxes of the alkaline carbonates, bisulphate of potassa, fluoride of ammonium, &c.

Platinum dishes are used with great advantage for evaporation, to heat or boil substances with strong acids (sulphuric acid) or with solutions of the caustic alkalies, for dissolving by means of hydrofluoric acid, possessing as they do the inestimable property, in all accurate operations, of not being acted upon by these bodies.

On the other hand the following bodies must not be treated in platinum vessels:

1. The caustic alkalies as well as baryta and strontia and their nitrates at a red and a melting heat.
2. Fusible metallic sulphides or mixtures of sulphates with carbon; thus in particular the alkaline sulphides.
3. Phosphates and carbon, which at a red heat give rise

to phosphide of platinum.

4. Metals that are easily fused, or mixtures of their oxides with substances which reduce them (carbon). These form with platinum fusible alloys.

5. Chlorine and all mixtures which liberate chlorine either in the cold or by heat, for instance, fusible mixtures of a metallic chloride and a nitrate, of sulphate of ammonia and chloride of ammonium. Furthermore manganates, permanganates and hydrochloric acid.

Platinum vessels are cleaned with borax or bisulphate of potassa, which is fused in them, they are afterwards digested in dilute acid, or scoured with fine round sand (sea sand) and water.

Silver crucibles are scarcely used for any thing else than for the fusing of the hydrate of potassa or of soda (separation of alumina from the oxide of iron, &c). They must be capacious and strong, and they require much care when raised to a red heat, on account of the easy fusibility of the metal, which naturally must be quite pure. If they are brought into contact with dilute hydrochloric acid, a certain amount of silver is dissolved.

IV. Balance and Weight.

One of the most indispensable instruments for the chemist is an accurate balance. For the analysis of inorganic substances a balance, when loaded with thirty grammes on either side and still turns with one milligramme, is sufficiently sensitive.

It is placed firmly in position where it can be protected both from dust and moisture. In order to fix it in a horizontal position it is furnished with adjusting screws and a spirit level.

When properly adjusted, the oscillations of the beam, which may be observed on a graduated index fixed behind the apex of the tongue, must be equal on either side of the zero point.

Amongst the precautions to be observed in reference to the use of a balance, may be mentioned, that neither a weight nor a vessel must ever be placed on the pan of the balance or

removed from it, as long as the beam is not fixed (that is, the motion of the beam is arrested, which generally is effected by some contrivance attached beneath the pans). Furthermore all violent agitation, every current of air must be avoided whilst weighing. A *hot vessel* must never be placed in the balance, because the weight in this case would not be accurate.

The weights, in general use among analytical chemists, are French and belong to the decimal system. The standard unit of these weights is the gramme (gm.), that is, the weight of a cubic centimetre of pure water at its greatest density, that is, at a temperature of 39.39°F. Its equivalent weight is 15.434 grains (Apothecary's weight).

A gramme is divided into 10 decigrammes, 1 decigramme into 10 centigrammes, and 1 centigramme into 10 milligrammes.

All expressions of weight are put down in the form of a decimal, in which the number of units before the period indicates the number of grammes, whilst the first unit figure to the right of the period expresses the decigrammes (tenths of a gramme), the second the centigrammes (hundredths of a gramme), and the third the milligrammes (thousandths of a gramme).

For instance, if a substance weighs 14 grammes 9 decigrammes 3 centigrammes and 5 milligrammes, it is expressed as follows: 14.935 gm. If one of the intermediate parts is wanting, its place is occupied, of course, by a cipher.

It is not at all necessary that the weights should be absolutely what they stand for, that is, that the gramme should be in reality equal in weight to a cubic centimetre of water, but *relatively* to each other they must be most accurate, and in due correspondence throughout, from which it is to be understood, that any weight, either slightly more or less than a gramme may be assumed as the standard unit, and that this must be equal to 10 other weights *exactly*, each of which is *mutually equal*, &c.

When gases have to be weighed, it is then absolutely ne-

cessary to make use of the real French gramme as a standard, because the weight of gases is based on certain fixed volumes.

It is of great importance to be careful in writing down the ascertained weights; for a single fault in this respect renders the whole analysis useless; and there are no means of controlling it.

For the analysis of a substance it is not customary to weigh out exactly one or two grammes, because this method would take up very much time, and it is almost just as easy to compute the result of the analysis with any other quantity.

It is no easy matter to determine in general the quantity of substance to be used in a given analysis; as a rule from one to two grammes will be sufficient. It is only when one of the constituents in a given substance exists in a very small quantity, and from its nature a further investigation becomes necessary, that a larger quantity is to be operated upon. Most substances are weighed out in vessels, for which purpose platinum vessels are the best, since the substances generally have been previously reduced to a fine powder and in this state dried, and in consequence are apt quickly to attract more or less moisture. But such bodies, where this is not to be apprehended, and which in general are presented in more compact masses, as for example alloys, may be weighed alone in the balance.

In the weighing of substances contained in a vessel, as for instance, in a platinum crucible, it is a general rule first to weigh the substance and the vessel together, and then when the substance is transferred to another more suitable for the further analysis, to weigh the crucible alone, because it frequently happens that a small quantity of the substance adheres to the crucible and would thus increase its weight. The difference of the two weights gives accurately the quantity used in the analysis. But, if the substance is easily soluble in the solvent to be employed, as for instance, a salt in water, the crucible is first weighed, afterwards the crucible and substance together; the latter is then poured out, and

the crucible is washed out with the solvent, which is added to the contents.

V. Analysis by Measure.

VOLUMETRIC METHOD.

The alkalimeter of Descroizelles is the type of all the methods of analysis, according to which the amount of a body is determined from the volume of a solution of some reagent of known strength, which liberates the body either in the form of gas, or of an insoluble combination, or gives rise to a certain color in consequence of oxidation or reduction. This branch of analytical chemistry owes its development especially to Gay-Lussac (alkalimetry, chlorimetry, the determination of silver), to Marguerite (analysis of iron by means of the permanganate of soda), and to Bunsen (the determination of iodine), and has already arrived at such a degree of perfection, that the volumetric determinations of substances are employed not alone for technical, but also for the most accurate scientific analyses, and are in a very high degree to be recommended owing to the shortness of time required in the operations.

The first and most important requirement is the preparation of a solution of the reagent, which contains an accurately known quantity of the same in a given volume of the solvent. The standard volume in use is the cubic centimetre (c. c.), which is divided into halves (0.5), or into fifths (0.2), or into tenths (0.1). The volume occupied by 1000 c. c. is called a litre. The amount of the effective reagent contained in a given volume of fluid is called its standard strength, and the fluid itself is denominated the standard solution. The preparation of a standard solution depends upon the nature of the reagent and may be made in two different ways. By the first method an accurately weighed amount of the reagent is dissolved in a so-called volume-vessel (flask, cylinder), that is, in a vessel containing a given volume, one litre or more, up to a mark on the neck or side of the vessel. This mode

of determining the volume is sufficient as far as regards technical operations; but for scientific purposes, and particularly in those cases where the substance can not be weighed with exactness, the strength has to be determined by special experiments much more accurately. (Vide Bunsen's process for determining the amount of iodine). This method consists in preparing a fluid whose strength is not fixed, or merely approximatively known, and then in arriving at accurate results by special experiments (vide determination of the standard acid in alkalimetry, and of the permanganate of potassa in the iron analysis).

The strength must not change in the course of time. But if such a change does take place, although to a trifling amount, it has again to be determined from time to time; but if the change is more appreciable, the adjustment must be made either before or after each analysis.

The final reaction is denominated the visibly perceptible appearance indicated by the completion of the reaction, that is, the point at which any further addition of the reagent must cease. A change of color is the most appropriate for this purpose, that is, either the commencement of a color or its disappearance; consequently reagents are used whose colors are definite and intense (permanganate of potassa), or a substance is added which produces a colored combination with the smallest possible excess of the reagent (starch paste for iodine, litmus for acids and alkalies).

The vessels, in which the standard solution of the reagent is contained, and from which it is allowed to pass out either in a stream or drop by drop, when required, are long narrow cylinders of glass drawn out at the bottom into a point and called burettes. They are graduated, naturally, into cubic centimetres and their fractional parts, and are in connection at the top with a larger reservoir, from which they can easily be filled with fluid in some convenient way. Those, which are supplied at the lower end with compressor stopcocks, are called compressor burettes, instruments first introduced by

Mohr; they allow the passage to be closed by compressing a small tube of indiarubber attached to the elongated narrow orifice at the bottom of the tube; there are others which are supplied with glass stopcocks and other modes of closing the lower orifice and regulating the outlet of fluid. But all these forms have their faults; and stopcocks of infallible perfection remain yet to be invented. The reading of the height of the fluid, before and after the experiment, is effected by placing the eye on a level with the surface of the fluid; but more accurately by means of a small glass tube, hermetically sealed, and containing a small quantity of mercury which causes the tube to sink in the standard solution. This plan was first suggested by Erdmann, and the tube has a horizontal line inscribed around its surface, and the coincidence of this line with one of the graduated lines on the outer tube is very easily observed. Such burettes are called swim-burettes.

1. Alkalimetry and Acidimetry.

The object of this analysis is to obtain the amount of alkali in aqueous solutions and in their carbonates, as also the amount of free acid in acid liquids, in all cases in which one equivalent of base unites with one equivalent of acid to form a neutral combination. The following reagents are required:

1. *Sulphuric acid.* One part of English sulphuric acid is diluted with ten or twelve of water, and in this condition is kept in stock.

2. *Solution of soda.* It must be free from carbonic acid, and preserved in well stoppered bottles to which carbonic acid can not get access. It must be diluted and have a specific gravity of about 1.1.

3. *Tincture of litmus.* The aqueous extract of litmus, which after filtration has been freed from any excess of base by means of a little acetic acid, until the solution assumes a violet color; it is kept in an open vessel.

Before use we must determine the strength of the sulphuric acid, and then the relative strengths of the sulphuric acid

and the soda solution. This is determined in the following manner: Pour a certain volume (from 20 to 50 c.c.) of the acid into water colored with a few drops of the tincture of litmus, and then place the vessel under the soda burette, and allow so much of the soda solution to flow into it until the last drop changes the red color to blue. (It is very convenient in practice, although not necessary, to make the strength of each fluid equal, that is, that one cubic centimetre of the acid shall neutralize one c.c. of the soda solution; this is easily accomplished by diluting either one or the other of these two fluids.)

In order to determine the absolute standard of the dilute sulphuric acid, from one to two grammes of pure carbonate of soda are placed in a covered platinum crucible and raised to a red heat (not fused), it is then weighed, dissolved in a flask in water, colored with a few drops of the tincture of litmus, and then placed under the acid burette, until the fluid becomes red. The fluid is now heated almost to boiling in order to expel any free carbonic acid, and then a trifling excess of acid is added to produce a permanent color. This is effected by placing the solution under the soda burette, from which so much soda solution is admitted as to reproduce the blue color. The amount of soda solution used gives that of the excess of acid, and by deducting this from the total amount of acid used, there remains the quantity which was required to neutralize the carbonate of soda. These experiments must be several times repeated, in order to obtain accurate results.

One equivalent of sulphuric acid(=40) saturates one equivalent of soda (=31), or one equivalent of hydrate of soda (=40), or one equivalent of protocarbonate of soda (=53).

Supposing it has been ascertained, that one gramme of carbonate of soda requires ten cubic centimetres of acid, then 100 cubic centimetres of the acid will saturate ten grammes of carbonate of soda, or 7.547 grammes of hydrate of soda, or 5.85 grammes of anhydrous soda.

Since the equivalent of potassa is 47, of the hydrated potassa 56, and of the carbonate of potassa 69, then 100 cubic centimetres of this acid will saturate 13.019 grammes of the protocarbonate of potassa, or 10.566 of the hydrate of potassa, or 8.87 of the anhydrous potassa.

From this the strength of the dilute acid in anhydrous acid, or the hydrated acid ($\text{SO}_3 + \text{HO} = 49$) is determined as follows:

$$53 : 40 :: 10 : 7.547^*$$

$$53 : 49 :: 10 : 9.245$$

Thus 100 cubic centimetres of the acid are found to contain 7.547 grammes of the anhydrous acid, or 9.245 grammes of the hydrated acid.

2. Volumetric Analysis with Permanganate of Potassa.

This reagent is a dilute solution of permanganate of potassa, the best being that which is pure and crystallized. It must not contain a trace of free potassa, nor too much chloride of ammonium. It owes its application to its powerful oxidizing properties and its intense color.

In order to obtain the standard strength of the solution, from one to two grammes of pure soft iron, free from rust, are dissolved (protected from all access of air, for instance in a flask provided with an india rubber valve,) in hydrochloric acid, to which previously a few pieces of marble have been added. This solution is poured into from 20 to 30 litres of water, and then so much of the chameleon solution is added, until the last drop communicates a slight but distinct red color to the whole solution. This experiment is repeated several times.

Instead of metallic iron a weighed quantity of the double sulphate of iron and ammonia ($\text{AmS}_3 + \text{FeS}_3 + 6 \text{ Aq}$) may be used. This is dissolved in water, and, as in the preceding experiment, is rendered quite dilute; it is then made slightly acid with hydrochloric acid placed beneath the burette containing the solution of permanganate of potassa. The salt

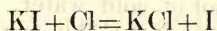
* Dilute sulphuric acid contains exactly the same amount of anhydrous sulphuric acid as of the hydrate of soda, their equivalents being equal (=40).

must have been recently prepared, pulverized and quite dry. Seven parts of this salt contain exactly one part of iron.

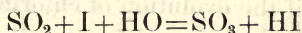
Obs.—The solution of permanganate of potassa may be kept unchanged for a pretty long time; nevertheless it is well, after the lapse of some time, to determine its contents again. India rubber must not be used to close the aperture of the burette.

3. Bunsen's Volumetric Analysis with Iodine.

This excellent method is used for determining the amount of oxygen, chlorine, &c.; it consists in allowing the latter direct, the former in the form of an equivalent of chlorine, to act on a solution of iodide of potassium, by which one equivalent of iodine is set free.



The amount of iodine is determined by an aqueous solution of sulphurous acid.



But since such a solution is constantly changing in strength, the latter must be determined for each analysis.

The requisite reagents are as follows:

1. *Sulphurous acid.* From 70 to 80 cubic centimetres of a saturated aqueous solution are diluted to ten litres.

2. *Solution of iodine.* Twenty grammes of pure dry iodine and 200 grammes of iodide of potassium are dissolved in six litres of water. One cubic centimetre of this solution contains therefore 0.005 grammes of free iodine. But as iodine is not always pure and dry, and can not easily be accurately weighed by reason of its volatility, the amount of the iodine in the solution must be controlled in an especial manner (for scientific purposes) as follows.

Pure recrystallized chlorate of potassa is pulverized to a fine powder and dried at a temperature of 392°F. An accurately weighed quantity (about 0.1 grm.) is placed in a flask connected with tubes with two Wolfe's bottles. The first and the larger of the two contains a solution of 3 grammes of io-

dide of potassium, filling it with this solution up to one-fourth or one-third of its volume; and the tube dips a few lines into the fluid. The second bottle contains only a small quantity of the solution of iodide of potassium. The flask is most conveniently closed with a stopper of indiarubber through which the narrow glass tube passes. As soon as all the connections are made, dilute hydrochloric acid is poured upon the chlorate of potassa, and the aperture is closed as quickly as possible. The solution is now heated, but quite gradually, lest the chlorine should be evolved too rapidly; it is afterwards made to boil, and the boiling is continued until all the chlorine has been driven off. Since the fluid in the first bottle becomes heated by the steam eliminated in the flask, the bottle is placed in a vessel of cold water. The iodine set free dissolves in the excess of iodide of potassium and gives rise to a brownish red solution. The contents of the second bottle remain colorless, if the evolution of chlorine is not too rapid. In order to complete the experiment, the stopper is taken out of the flask whilst the contents are still boiling; and the solution of iodine is placed in a beaker glass, to which is added sulphurous acid from a burette, stirring all the while, until the fluid has lost all its color, after which about 5 cubic centimetres more of the sulphurous acid (up to the next graduated line) are added. It is now mixed with a little thin starch paste and then placed under the iodine burette from which a sufficient quantity is allowed to flow so as to produce a distinct blue color.

After the completion of this experiment the relative strengths of the two solutions, namely, of sulphurous acid and of iodine are determined as follows: a fixed quantity, say 50 cubic centimetres of the former are poured into water, to this a few drops of starch solution are added, and the solution is finally placed beneath the iodine burette as before.

In this way the strength of the iodine solution is determined.

From one equivalent of chlorate of potassa ($=122.5$) six equivalents of chlorine are evolved, which set free 6 equiva-

lents of iodine ($= 762$). If one gramme of the salt has been used, 0.622 grm. of iodine will be set free.

Supposing the result of the second experiment shows, that 5 cubic centimetres of sulphurous acid were equal to 1 cubic centimetre of the solution of iodine, and that there were in the first experiment 630 cubic centimetres of sulphurous acid and 1 cubic centimetre of the iodine solution, the excess of the former would have been equal to 5 cubic centimetres, the free iodine therefore would have required only 725 cubic centimetres of sulphurous acid. Since now

$$5 : 1 :: 625 : 125$$

therefore, 125 cubic centimetres of the iodine solution contain just as much iodine as the quantity obtained by means of 0.1 gramme of chlorate of potassa, that is, 0.622 gramme. Since now

$$125 : 0.622 :: 100 : 0.4975$$

therefore

100 c.c. solution of iodine contain 0.4975 gramme.

1

"

0.004975 "

of iodine, instead of 1 c.c. " containing .005 " as it should have been.

The solution of the sulphurous acid accordingly contains only 0.025 per cent of the latter. According to Bunsen its strength must not be higher than from 0.03 to 0.04 per cent.

The strength of the iodine solution must be repeatedly tried in order to attain the greatest certainty.

I. Metallic Alloys.

Under this head are comprehended all substances, composed of metals in the reguline condition, with the exception of arsenic, whose combinations with other metals will be treated of in a special section further on.

Of minerals, therefore, will be comprehended here: amalgams, antimonial silver, meteoric iron; to a much greater ex-

tent, however, all the artificially prepared alloys, as gold and silver coins, brass, bronze, cannon and bell metal, German silver, soft solder and other fusible combinations, type-metal, as well as those metals produced by metallurgic processes which, as a rule, are accompanied with others, copper, tin, zinc, lead, silver, nickel, &c.*

These bodies we divide into two classes in reference to their comportment with nitric acid: First, those which are completely soluble in nitric acid; and, secondly, those which are perfectly insoluble in this acid. To the latter belong all alloys containing tin, antimony and gold.

The most suitable solvent for alloys is nitric acid, which converts almost all the metals into soluble nitrates; but gold platinum and a few other metals of more rare occurrence are not dissolved by this acid. Tin and antimony, however, although they are oxidized by this acid, give rise to insoluble oxides; tin being converted into the insoluble tannic acid, whilst antimony, according to the strength of the acid and the continuance of its action, is converted into the teroxide of antimony, antimonite of antimony (formerly, antimonious acid), and antimonic acid, of which one part is soluble, whilst the other remains behind, thus rendering the accurate determination of the metal very difficult.

The nitric acid to be used as a solvent must be free from chlorine if the alloys contain any gold, silver, lead, tin or antimony. In other cases its presence does no harm; on the contrary, it sometimes happens that aqua regia must be used for the solution of certain alloys.

Alloys containing much silver or lead are not so easily affected with a very concentrated nitric acid, as with a more dilute acid, from the fact, that the nitrates of these metals are insoluble in the acid itself.

* The analysis of crude iron, bar iron and steel will be found in another section.

A. ALLOYS, WHICH ARE SOLUBLE IN NITRIC ACID, THAT IS, WHICH CONTAIN NEITHER GOLD, TIN NOR ANTIMONY.

1. SILVER AND COPPER.

(SILVER COINS.)

Place a suitable quantity of the substance (from one to two grammes) in a small flask or beaker glass, and cover it with a moderately strong *pure* nitric acid, warm the flask over the lamp, or the beaker glass, covered with a piece of concave glass, in the sand-bath, and continue the digestion until the solution is complete. The solution is then diluted with water and poured into a beaker glass if the operation had been performed in a flask, otherwise it is continued in the same beaker glass. In the former case the flask is thoroughly washed with water, which is added to the solution.

The silver is precipitated out of the solution by means of hydrochloric acid, which is added drop by drop, stirring all the while, as long as a precipitate is produced. The solution is then set aside in a gentle heat until all the precipitated chloride of silver has settled to the bottom and the supernatant fluid is quite clear. In the meanwhile a filter sufficiently large for the precipitate is placed to dry at a temperature of 248°F. (instructions for doing this are given on page 29), and through this the clear solution is filtered into a capacious dish, having first tested it with a few drops of hydrochloric acid to ascertain the complete separation of silver. The fluid portion is poured first on the filter, and the chloride of silver is stirred up with a little water and poured next; the beaker glass is thoroughly cleaned by means of the washing bottle and a feather, and the wash-water filtered. It is well to add a few drops of nitric acid to the wash-water in order to prevent any chloride of silver from passing through the filter and thus rendering the filtrate turbid. The same addition of nitric acid is to be recommended when the mass of chloride of silver on the filter is washed with hot water, but only at the beginning; afterwards pure water alone is used, and

the washing is continued until the filtrate no longer shows an acid reaction, nor leaves any deposit when evaporated to dryness.

Vide page 23 concerning precipitating, page 27 about filtering, and page 32 in relation to washing.

The washed filter together with the chloride of silver is dried (vide page 33), then placed in a platinum crucible and put to dry in the drying apparatus (vide page 34), and the residue is then weighed, and from this the quantity of the silver is computed.

Add *carbonate of soda* to the copper solution in the dish until it has only a faint acid reaction. The operation is performed as follows: add the crystallized salt in small portions at a time gradually and stir the solution after each addition until the salt is dissolved, and then add fresh crystals. Cover the vessel with a glass plate in order to prevent loss by the evolution of carbonic acid: the glass cover is finally washed with the washing bottle. As soon as the point has been attained when the fluid has just a slight acid reaction, and the incipient precipitate again dissolves on stirring, the dish is heated over the lamp, and when the fluid is hot, a solution of caustic potassa is added until it has a distinct alkaline reaction; it is then raised to a boiling temperature, stirring it all the while, until the precipitate becomes brown-black. When sufficiently cool the contents of the dish are filtered, the dish is carefully cleaned from all adhering oxide of copper, and the latter is thoroughly washed on the filter with hot water.

The filtrate from the oxide of copper is tested with hydrosulphuric acid for any remnant of copper. Sometimes a small quantity is found. In this case the precipitate is placed in a covered vessel to settle, the fluid portion is poured off, and the residue is filtered and washed in a small filter, dried and raised to a strong red heat under free access of air. It is now oxide of copper which is weighed and added to the larger quantity.

OBSERVATION. — The addition of carbonate of soda is intended to remove the largest portion of the free acid, in order not to require so much potassa, which is rarely

ever pure, and which consequently produces a larger quantity of potassa salts, that are not so easily removed as the corresponding soda salts. The oxide of copper must never be precipitated out of very concentrated solutions, because it is somewhat soluble in a concentrated solution of potassa and adheres tenaciously in part to the dish. In such a case it may be removed by a few drops of hydrochloric acid and a dilute solution of potassa with the aid of heat. It requires considerable time before the washing is complete.

As soon as the oxide of copper has been well dried in the air (vide Drying, page 33), it must be heated to a red heat according to instruction, page 34, taking especial care to admit free access of air, because a part is easily reduced by the charcoal to the state of the dinoxide, and it must be weighed in the covered crucible as soon as it is cold. From this weight the amount of copper is computed.

2. COPPER AND ZINC.

(BRASS, SIMILOR, PINCHBECK, TINSEL OR FALSE GOLD LEAF, AND BRONZE FREE FROM TIN.)

The substance is dissolved in the same manner precisely as in the preceding example, only here be it observed, that it is no disadvantage whatever if the nitric acid should contain chlorine. In fact the alloy may first be covered with hydrochloric acid, a little nitric acid then added, the whole heated, and then more of the latter acid may be added until the solution is complete. The resulting compounds in this case are chloride of copper and chloride of zinc instead of nitrates of the same metals.

The acid fluid is diluted with sufficient water in a beaker, and a current of hydrosulphuric acid is passed through it, taking care to cover the vessel with a plate of glass. This operation is continued until all the copper is precipitated, a fact recognized by the strong smell of hydrosulphuric acid after stirring the mixture and blowing away the air above the fluid with the breath from the mouth, or still more certainly by allowing the precipitate to settle, and the fluid to become clear, when the latter will appear quite colorless, and on the addition of a few drops of a solution of hydrosulphuric acid no more precipitate is produced.

As soon as all the copper has thus been completely preci-

pitated, the glass tube is disconnected from the indiarubber connector of the hydrosulphuric-acid-generating apparatus, and left in the beaker glass; the sulphide of copper is then filtered and the filtrate is received in an evaporating dish.

The filtering of sulphide of copper (as also of several other metallic sulphides, for example, of zinc, iron, nickel, cobalt) requires many precautions. Like them it is endowed with the property, in the moist condition, of attracting oxygen from the air, whereby it becomes sulphate of the oxide of copper.

To obviate this the filtration must be performed with rapidity, and without access of air. Therefore not only must the filter be covered with a plate of glass, but the beaker glass, which contains the precipitate, must be similarly protected. As soon as the contents of the filter have been passed through, a fresh supply must be immediately poured upon it, and the funnel kept full until the precipitate itself is completely on the filter. Particles, which adhere to the beaker glass, to the covers or conducting tube must be removed with the wash-bottle and a feather and also placed on the filter, and the residue is finally washed for a short time with cold water containing a few drops of hydrosulphuric acid.

If the necessary precaution be neglected, the portions of fluid, that pass through last, will produce a turbidity in the filtrate, arising from the fact that these last portions carry down a solution of the sulphate of the oxide of copper produced by the oxidation of the sulphide, which, coming in contact with an excess of hydrosulphuric acid in the filtrate, again produces a precipitate of the sulphide of copper. In this way the operation is a failure, and must be repeated.

Since the precipitate of sulphide of copper, on account of its liability to change when exposed to air and warmth, is not appropriate for the direct determination of the copper, it must be converted into a sulphur compound corresponding to a protoxide, which is unchangeable. The precipitate is dried, rubbed from the filter and poured into a weighed porcelain crucible; the filter together with any adhering particles of the

precipitate is burned on the cover of the crucible, and the ashes are then added to the sulphide in the crucible; now add a few centigrammes of the flowers of sulphur and mix it with the rest. The crucible is then covered with a lid to which is attached a bent porcelain tube, intended to conduct dry hydrogen gas into the crucible, which is placed over a lamp and gradually heated to redness as soon as the atmospheric air has been removed by the hydrogen. The contents of the crucible are allowed to cool beneath an atmosphere of hydrogen. In this way pure disulphide of copper, Cu_2S , is obtained, and this is weighed and the copper therefrom computed.

We now come to the fluid separated by filtration from the sulphide of copper, containing the zinc in solution. This is first evaporated in order to concentrate it, and to remove all excess of hydrosulphuric acid. *Chrystallized carbonate of soda* is now added gradually, stirring the mixture all the while, until all effervescence ceases; a precipitate is thus produced and the fluid has an alkaline reaction. During this operation the vessel is covered with a plate of glass to prevent loss by the spurting of the carbonic acid, and the plate itself is afterwards cleaned with the washing bottle. The fluid is next raised to a boiling temperature, the carbonate of zinc which is precipitated is then removed by filtration and washed with boiling water. The precipitate is dried and heated to a high red heat, in order to remove the carbonic acid and thus produce pure oxide of zinc. The burning of the filter to ashes is performed in the same way as with that containing oxide of copper, only there is less fear of the reduction of the metal. The oxide of zinc is then weighed and the amount of zinc computed.

OBSERVATION 1. — The fluid, filtered from the precipitated carbonate of zinc, is tested by a few drops of sulphide of ammonium to see if it is free from zinc. If a precipitate is produced, it is allowed to subside in a covered beaker glass; the clear supernatant fluid is poured off, and the residue is filtered and washed in a funnel covered with a glass plate; it is afterwards digested together with the filter, whilst still moist, with a little hydrochloric acid in a beaker glass, until the smell of hydrosulphuric acid has been removed; the solution is then diluted, filtered into a dish and again precipitated as before with carbonate of soda.

OBSERVATION 2. — A portion of the zinc oxide, after it has been weighed, is

tested for the presence of any carbonic acid, which might still remain if the carbonate had not been heated long enough. It is moistened with water and then hydrochloric acid is added which ought to produce no effervescence.

Sometimes it happens that the oxide of zinc has a yellow color; this arises in general from a very small quantity of iron which is seldom absent in such alloys. If it is desired to determine the amount of iron, the oxide of zinc that has been heated to a red heat and weighed, is placed in a beaker glass, dissolved in dilute hydrochloric acid and supersaturated with ammonia. The oxide of iron is precipitated, and is separated by filtration, thoroughly washed, dried, heated to a red heat and weighed. From this the amount of iron is computed and deducted from the preceding weight of the oxide of zinc, which in general may be neglected.

3. COPPER ZINC AND NICKEL.

(GERMAN SILVER, ARGENTAN, PACKFONG.)

The operation at the beginning is precisely the same as in preceding example, the copper is precipitated from the acid solution by hydrosulphuric acid, and converted into the disulphide. The fluid portion filtered from the sulphide of copper containing the zinc and nickel is, in like manner, concentrated by evaporation, in order to separate the remaining traces of hydrosulphuric acid. It is next supersaturated in a flask with pure hydrated potassa, and afterwards sufficient hydrocyanic acid is added so as to convert the whole into a yellow fluid. From this solution of the double cyanides the zinc is precipitated as sulphide of zinc by the common sulphide of potassium (prepared from the sulphate of potassa by means of charcoal); the mixture is set aside to digest and settle; it is then filtered in a covered filter into a flask; the precipitate is washed in cold water containing a little sulphide of potassium, and dissolved in a covered beaker glass by digestion in hydrochloric acid, until the smell of hydrosulphuric acid has been entirely driven off; the diluted solution is filtered into a dish; and the oxide of zinc precipitated by carbonate of soda as in the preceding example.

The filtrate from the sulphide of zinc is boiled in the flask with aqua regia, until all smell of hydrocyanic acid and hydrosulphuric acid has been expelled and does not return on the addition of acid; the solution is then supersaturated in a dish with hydrate of potassa and kept boiling for some minutes. The hydrated oxide of nickel is then filtered from

the solution, washed in hot water, dried, heated to redness and weighed; the weight of the nickel is computed from the amount of the oxide.

The direct determination of the nickel may be omitted; in this case the fluid separated from the sulphide of copper, after all hydrosulphuric acid has been removed, is treated with an excess of carbonate of soda at a boiling temperature (as in the precipitation of the zinc); the mixed oxide of zinc and of nickel on the filter is washed, dried, heated to a red heat and weighed. It is next placed in a flask and dissolved in hydrochloric acid, potassa is then added, afterwards hydrocyanic acid and so on, as before. The amount of the oxide of nickel is then obtained by the difference of weights.

4. LEAD AND ZINC.

The alloy is dissolved in moderately strong nitric acid, and to the solution is added the proper amount of sulphuric acid; the mixture is evaporated until the excess of sulphuric acid begins to pass off, it is now allowed to cool, is then diluted with water containing one-fourth its volume of alcohol and filtered on paper dried at 248°F . The precipitated sulphate of lead is thoroughly washed and dried. As soon as it is dry it is placed, together with the filter, in the drying apparatus at a temperature of 248°F ., and left there until its weight becomes constant.

The filtrate collected in a dish is evaporated until all the alcohol is driven off, and then the oxide of zinc is obtained according to instructions, page 53.

5. COPPER AND BISMUTH.

The solution in nitric acid is evaporated to a small volume, mixed with hydrochloric acid and diluted with much water. By this the basic chloride of bismuth ($\text{BiCl}_3 + 2\text{BiO}_3$) is separated completely. The complete separation depends solely on the right proportion between the acid and the water. The greater the quantity of acid present, the greater the quantity

of water to be added. The deposit, therefore, is allowed to settle, and the supernatant fluid is tested with an addition of water.* The precipitate is either placed on a weighed filter, so long washed with cold water until the drainings no longer show any acid reaction and finally dried at the temperature of boiling water, or it is collected on an unweighed filter, and after drying melted in a covered porcelain crucible with five times its weight of cyanide of potassium (the filter being placed on the top and covered with cyanide of potassium). As soon as the crucible is cold, it is immersed in a dish of warm water; and the bismuth, that has been melted into fine globules, is washed first in water, afterwards in alcohol, it is then dried and weighed. (If a part has been reduced in the form of a black powder, it is melted over again with cyanide of potassium, and so on as before.)

The filtrate containing the copper is evaporated to a suitable volume, then sufficient carbonate of soda is added to still leave the fluid slightly acid, and afterwards a small quantity of aqueous sulphurous acid. The mixture is set aside for a few hours either in a cold place or where it is gently warmed. Hereupon the copper, reduced by this proceeding to the state of protoxide, is precipitated by a concentrated solution of sulphocyanide of potassium; the precipitate is allowed to settle, and the fluid is tested again with the reagent. The precipitate of sulphocyanide of copper, Cu_2CyS_2 , is collected on a weighed filter, washed in cold water and dried at a temperature of 212°F .

6. LEAD AND BISMUTH.

The solution in nitric acid is reduced by evaporation to a small volume, and then mixed with a small quantity of water and with hydrochloric acid so as to retain all the bismuth and the lead in solution, if the latter is not present in too great a

*Very acid solutions of bismuth must be freed from their excess of acid either by evaporation, or by a partial neutralization with an alkali. When free nitric acid is present, either chloride of sodium or chloride of potassium is used to produce precipitation, instead of hydrochloric acid.

quantity, in which some chloride of lead is separated. In order to ascertain the right quantity of hydrochloric acid, a little of the fluid is mixed with water. If a single drop produces turbidity, more acid must be added. When this has been done, the clear fluid is poured into a beaker glass (any chloride of lead that may have been separated may, according to its quantity, be either dissolved in water by boiling, or be placed on a weighed filter, washed with dilute alcohol and dried at $248^{\circ}\text{F}.$), and the lead is precipitated by the addition of moderately dilute sulphuric acid, and the mixture is set aside for some time to settle. After this, alcohol, spec. grav. 0.8, is added and the mixture is again allowed to settle; the precipitated sulphate of the oxide of lead is then separated by filtration, washed with alcohol containing a small quantity of hydrochloric acid, finally with pure alcohol, and treated afterwards according to instructions, page 55.

The bismuth in the filtrate is precipitated as the basic chloride by means of a large quantity of water. Since the precipitate contains traces of sulphuric acid, it is reduced by very accurate manipulations with cyanide of potassium (vide page 56).

7. COPPER, LEAD, ZINC.

The nitric acid solution is evaporated according to instructions, page 55, with sulphuric acid; and the lead is determined as sulphate of the oxide of lead.

The alcohol is expelled by heat from the filtrate in an evaporating dish; and then hydrosulphuric acid is passed through it. Vide, for the rest of the treatment, page 51.

B. ALLOYS, WHICH ARE NOT COMPLETELY SOLUBLE IN NITRIC ACID.

1. TIN, COPPER.

(BRONZE, BELL-METAL, CANNON-METAL, &c.)

1. METHOD.

The alloy is first reduced into the smallest pieces possible and then digested in moderately concentrated nitric acid, sp. gr. 1.3, free from chlorine, until the metallic parts are oxidized; the fluid portion, together with the deposited stannic acid is put into an evaporating dish and evaporated to dryness on the water bath; the dish is then placed over the flame of a lamp, and the temperature is raised until a portion of the nitrate of copper begins to be decomposed, liberating the black oxide of copper; it is now set aside to cool and then moistened with nitric acid until the black oxide again disappears; after diluting the residue, the stannic acid is removed by filtration, and washed in several waters until it no longer shows an acid reaction. When perfectly dry the stannic acid is rubbed from the filter and poured into a porcelain crucible; the filter itself is incinerated on the cover of the crucible, and the ashes are added to the contents of the crucible, which are now moistened with nitric acid, then heated and finally ignited. The amount of tin is computed from the weight of the stannic acid.

The copper is precipitated from the filtrate by means of hydrosulphuric acid (vide page 51).

OBSERVATION. — The stannic acid may contain a trace of copper.

2. METHOD.

Proceed from the commencement as before until the mass is reduced by evaporation to dryness; the residue is then treated with hydrochloric acid and completely dissolved by the addition of water and the application of heat. The stannic acid is then precipitated by dilute sulphuric acid and allowed to settle; it is then filtered, washed, dried and ignited as before indicated. After ignition a small piece of carbonate of ammonia is placed within the crucible, which is covered up and heated a second time. The operation is repeated, after weighing, until the weight remains constant.

The copper is determined as already indicated.

2. TIN, LEAD.

(SOFT SOLDER, BLOCK TIN, TIN FOIL ALLOYED WITH LEAD, &c.)

The alloy is first oxidized with nitric acid, evaporated to dryness on the water bath; the residue is then heated at a higher temperature, moistened with nitric acid; and the stannic acid is separated as in the preceding example (first method). The filtrate is evaporated with the addition of sulphuric acid; and the lead is determined as sulphate of the oxide of lead (vide page 55).

3. TIN, LEAD, ZINC.

Analysis the same as in the foregoing, combined with No. 4 (page 55).

4. TIN, COPPER, LEAD, ZINC.

(SEVERAL SORTS OF BRONZE AND OF BRASS.)

In such alloys the amount of tin and lead is generally very small. The process is that of No. 1 (first method) and No. 2; after the separation of the stannic acid by filtration, the lead is removed from the filtrate by sulphuric acid, then the copper by hydrosulphuric acid, and finally the zinc by carbonate of soda (vide page 53).

TIN, LEAD, BISMUTH.

(FUSIBLE METAL, ROSE'S METAL.)

The alloy is first cut up into small pieces, and oxidized in a capacious flask with nitric acid; the solution is slightly diluted, saturated with ammonia in excess and digested for a considerable time with concentrated sulphide of ammonium to which is added a small quantity of sulphur, taking care to shake the mixture frequently. In this way the tin is dissolved as sulphide; the sulphides of lead and bismuth are separated by filtration and washed with cold water.

To the fluid, containing the sulphide of tin, is added dilute sulphuric acid in excess; and the vessel, loosely covered with

paper, is submitted to quite a gentle heat, until the contents no longer smell of hydrosulphuric acid. The yellow sulphide of tin is washed with cold water on the filter, and is then so far dried as to allow the filter with its contents to be removed from the funnel. The latter is then put, in the first place, in a covered porcelain crucible, which is afterwards opened, and exposed to a long continued gentle heat, until it no longer smells of hydrosulphuric acid. This point attained, the contents of the crucible are moistened with a few drops of nitric acid, and heated at first gradually with access of air, and finally ignited. The sulphide of tin is next changed into stannic acid, and afterwards treated with a little carbonate of ammonia (vide page 58).

The sulphides of lead and bismuth are dried and rubbed off from the filter which is incinerated; these ashes and the dried sulphides are digested with nitric acid (vide page 57), in order to separate these two metals.

6. TIN, LEAD, BISMUTH, CADMIUM.

(WOOD'S FUSIBLE ALLOY.)

The process begins the same as in the preceding example. After separating the bismuth by water as basic chloride, and evaporating the fluid to a suitable volume, the cadmium can be determined by two methods.

A.—Add carbonate of potassa in excess; the mixture is then heated; the carbonate of the oxide of cadmium is separated by filtration, washed, dried, rubbed off from the filter and placed in a porcelain crucible; the filter itself is incinerated on the cover of the crucible, and the ashes are added to the contents of the crucible; these are ignited and maintained at this temperature for some time in order to drive off the carbonic acid, which is no easy operation. The brown oxide of cadmium is now weighed, then moistened with a few drops of nitric acid, again ignited and weighed, in order to ascertain whether all the carbonic acid has been driven off.

B.—The cadmium is precipitated by hydrosulphuric ac-

id, the resulting sulphide is filtered on a weighed filter, washed with cold water, containing a little hydrosulphuric acid and hydrochloric acid, and finally dried at a temperature of 212°F. , until the weight remains constant.

7. TIN, LEAD, BISMUTH, MERCURY.

(FUSIBLE ALLOY.)

Proceed as in the two preceding examples. After the separation of the bismuth, the mercury is converted into the sulphide by hydrosulphuric acid; the latter is filtered on a weighed filter, washed with cold water, and dried at a temperature of 212°F. , until the weight remains constant.

8. ANTIMONY AND LEAD.

This alloy forms the metal denominated type-metal, but it sometimes contains a little copper and bismuth.

If antimony and lead alone are present, the alloy is divided up into very small pieces, and then digested in a flask with concentrated nitric acid, until the antimony is oxidized. The solution is then diluted; and ammonia in excess is added, and afterwards a concentrated solution of the yellow sulphide of ammonium to supersaturation. It is necessary that the latter reagent should be yellow,* because the solution of the sulphide of antimony takes place more quickly in the presence of free sulphur. If, therefore, the sulphide of ammonium has been recently prepared, a small quantity of the flowers of sulphur must be added. The whole is digested for a long time in the flask, and towards the end the mixture is heated nearly to the boiling point. The flask is finally removed from the heat, corked and set aside until the precipitate has subsided. The latter must be of a pure black color, whilst the supernatant fluid must be yellow; if this is not the case with either of them, too little of the sulphide of ammonium has been em-

*Sulphide of ammonium is prepared by passing a current of hydrosulphuric acid through a mixture of one part of ammonia and two parts of water, until the fluid no longer precipitates a solution of sulphate of magnesia. It becomes yellow by keeping through the formation of supersulphide of ammonium.

ployed, consequently more must be added and the digestion repeated. As soon as the solution is cold, the undissolved sulphide of lead is removed by filtration from the solution of antimony, washed thoroughly with cold water, dried and then placed in a weighed porcelain crucible; the filter is burned separately and the ashes are added to the sulphide; a quantity of sulphur is now mixed up with it and the whole is ignited in a current of hydrogen, in the manner in which sulphide of copper was treated (vide page 53). As soon as the crucible containing the sulphide of lead has been weighed, more sulphur is added and the ignition is repeated, in order to see whether the weight remains constant. The amount of lead is estimated from the quantity of sulphide of lead (PbS).

The solution of sulphide of antimony is decomposed by hydrochloric acid, adding it drop by drop and stirring the solution all the while, until it has a slight acid reaction, and then the vessel is covered with a plate of glass. By proceeding in this manner, the sulphide of antimony is precipitated. The mixture is digested at a gentle heat, until all smell of hydrosulphuric acid has disappeared, it is then filtered on a filter that has been dried at a temperature of 248°F. ; the precipitate is washed in several waters (cold), to which at the beginning a few drops of hydrochloric acid have been added, in order that the fluid may not be turbid as it passes through. After it has been dried in the air, it is maintained at a temperature of from 248° to 266°F. in the drying apparatus, as long as its weight changes.

From its weight, however, the amount of antimony can not be computed in a direct manner, since it is not alone a mixture of the two different sulphides of antimony, but in general contains also free sulphur. In order to ascertain the amount of antimony in the precipitate, as much as can be removed from the filter is placed in a weighed capacious porcelain crucible, and the filter, together with that portion of the precipitate still adhering to it, is dried again in order to ascertain the amount which has been taken out. The latter is first

moistened with a few drops of nitric acid, sp. gr. from 1.2 to 1.4, afterwards a larger quantity of acid, sp. gr. 1.5 is added: the crucible is then covered with a watch glass, heated on a water bath, and afterwards very gradually over the lamp to ignition. By this means the sulphides are converted into the combination of the two oxides, SbO_3 , SbO_5 , which remains as a white mass, from which the amount of antimony is computed. The ignition is repeated in order to ascertain whether the weight remains constant or not.

6. ANTIMONY, TIN.

The alloy is divided up into the smallest possible pieces and then covered with pure nitric acid in a beaker glass in which it is digested, until all has been oxidized; the contents are then placed in a porcelain crucible and evaporated to dryness; the residue is now heated, but not to ignition. It is now mixed with an excess of hydrated soda, and fused in a silver crucible and maintained at a red heat for some time. After cooling the residue is immersed in a large quantity of water containing one-third its volume of alcohol, sp. gr. .833. By this procedure the stannate of soda is dissolved, whilst the antimoniate of soda remains behind. The latter is removed by filtration, and washed at first with equal parts of alcohol (sp. gr. 0.833) and water, and afterwards with a mixture of three volumes of alcohol and one of water. The funnel is now fixed air-tight in the cork of a flask; and a mixture of hydrochloric acid and tartaric acid is poured upon the salt; the funnel is now covered up and set aside. As soon as the contents are dissolved, the fluid is allowed to pass through the filter, which is washed with the same mixture and finally with water. The antimony is next precipitated by means of hydrosulphuric acid; and the resulting sulphide of antimony is treated as in the preceding example.

The solution of stannate of soda is gently warmed, in order to drain off the largest portion of the alcohol, water is then added, and the solution is rendered acid with hydrochloric

acid. Finally the tin is precipitated with hydrochloric acid. The yellow sulphide of tin is converted into stannic acid (vide page 60).

II. METALLIC OXIDES.

1. ANALYSIS OF IRON.

In order to determine the amount of iron in a fluid the volumetric process with permanganate of potassa may be employed (vide page 44). If the fluid contains a salt of the *protoxide*, the volumetric process may be applied at once; if the solution contains a salt of the *sesquioxide*, the latter must first be reduced to the state of protoxide; and if finally salts of *both oxides* are present, two volumetric analyses are made: the difference between the two is that amount of protoxide which by computation must be changed into sesquioxide.

A.—Determination of the Sesquioxide.

The solution in hydrochloric acid is diluted in a flask, if it is very acid it is partially neutralized with carbonate of soda, and then reduced with zinc. This is effected by suspending a ball of zinc, attached to a platinum wire by casting, in the fluid; the wire is supported by a loosely fitting cork. In this condition the fluid is kept heated until it becomes colorless.

The ball is then taken out and rinsed; whilst the solution is poured into a large quantity of water and submitted to the action of permanganate of potassa from a burette.

B.—Determination of the Sesquioxide and the Protoxide.

Firstly (a).—A weighed quantity of the substance is dissolved in hydrochloric acid, and, in order to prevent all access of air, either a small piece of marble is dissolved with it, or the solution is made in a small flask furnished with an india-rubber valve. The solution is poured into a vessel of pure water,

and then submitted to the action of permanganate of potassa.

This experiment gives the amount of the protoxide.

Secondly (b).—A fresh quantity of the substance is dissolved in hydrochloric acid and treated as in article A. This gives the whole of the iron in the form of protoxide; from this the quantity found in the first part of B is deducted, and the difference, when multiplied by ten-ninths, will give the amount of sesquioxide in the substance.

If in a substance containing both the oxides of iron the whole amount of iron is determined, by precipitation with ammonia, as sesquioxide, then, naturally the first analysis(a) is all that is required. For, if the amount of protoxide found be multiplied by ten-ninths and the product be deducted from the total amount of sesquioxide of iron precipitated by ammonia, we obtain the amount of protoxide originally present in the substance examined.

2. BROWN HEMATITE, LIMONITE.

(SESQUIOXIDE OF IRON, CLAY, WATER.)

A.—A portion reduced to rough powder is ignited, and the loss of weight is determined. This loss gives the weight of the water.

B.—A quantity reduced to a fine powder is digested in hydrochloric acid until all, with the exception of the clay itself, is dissolved. To the acid solution is added ammonia in excess; the precipitate is removed by filtration, washed with hot water, dried, ignited and weighed as sesquioxide of iron.

In the filtrate may be found sometimes small quantities of lime (by means of oxalic acid) and of magnesia (by phosphate of soda). Vide Carbonates, for example, Spathic Iron Ore.

3. BOG IRON ORE.

Hydrated oxide of iron, and hydrated oxide of manganese, mixed with silicic acid, phosphate, sulphate and huminate of the sesquioxide and of the protoxide of iron, as also with

quartz-sand.*

Bog ores are impure brown hematite, in which the substances above-mentioned are not always present.

A—A weighed quantity in fine powder is dried over sulphuric acid in the drying apparatus (under a bell-shade of the air-pump) in order to determine the amount of hygroscopic water. The remaining results are computed in reference to the weight of the dried substance.

B—The powder, that has been dried in (A.), is heated in a platinum crucible, then ignited with access of air. The loss of weight consists of water and organic substances.

To determine the amount of each of these substances separately is of no use in practice; and besides this an organic elementary analysis would be required; we shall therefore proceed no further with them.

C—A weighed quantity of the ore is reduced to an impalpable powder and digested in an evaporating dish with hydrochloric acid (if chlorine is evolved, it indicates the presence of the oxide of manganese) and evaporated to dryness on the water-bath. When cold the residue is moistened uniformly with hydrochloric acid, after standing some time water is added, and the mixture is heated and then filtered. The insoluble residue consists of the silicic acid from the silicates present in the ore, and of quartz. After it has been thoroughly washed, dried, ignited and weighed, it is added gradually to a boiling concentrated solution of from 20 to 30 grammes of carbonate of soda, and is kept boiling for some time; the hot fluid is afterwards diluted and filtered; the filtrate contains the silicic acid, which has been separated from the silicates, whilst the residue is quartz; this is washed, dried, ignited and weighed. The amount of the silicic acid is obtained by taking the difference of the two weights. The solution in hydrochloric acid is supersaturated with ammonia. The preci-

*Sometimes also alumina, lime, magnesia, oxide of copper and arsenious acid. The presence of alumina together with phosphoric acid renders the analysis difficult. (Vide Phosphates, example 7.)

pitate is thoroughly washed, dried, ignited and weighed. It contains beside the oxide of iron also oxide of manganese and the phosphorus acids. In order to determine the amount of these substances, the residue is rubbed to a fine powder, then ignited and weighed; it is then mixed in a platinum crucible with from three to four times its weight of powdered dried carbonate of soda. This mixture is maintained for a quarter of an hour at a vivid red heat; the crucible, when cold, is placed together with its contents in water, in which it is left to soak. By the addition of alcohol and the application of heat the manganic acid produced is decomposed. The oxides of iron and manganese are now removed by filtration, well washed, dissolved, without removing the filter, in a capacious dish with hydrochloric acid to which a little alcohol is added; the whole is now pretty well diluted and gently warmed, whilst powdered carbonate of soda is gradually added (keeping the dish between whiles covered with a plate of glass), until a part of the oxide of iron is precipitated, although the fluid is still of a red color. A few grammes of acetate of soda are now added and the mixture is heated to boiling. The oxide of iron thrown down is filtered while hot, thoroughly washed, again returned to the dish, dissolved in hydrochloric acid and precipitated with ammonia. From the first filtrate manganese is precipitated by boiling with an excess of carbonate of soda. The carbonate of manganese is then obtained by filtration, washed, dried and ignited, with access of air, by which it is converted into the protoxide.

The only thing, that now remains to be done, is to determine the amount of phosphoric acid in the first filtrate from the oxides of iron and manganese. This filtrate is rendered slightly acid with hydrochloric acid in a covered beaker glass, and gently heated for some time in order to remove the carbonic acid, it is then supersaturated with ammonia and decomposed with a clear solution of sulphate of magnesia, chloride of ammonium and ammonia (magnesia mixture). The mixture is set aside for twelve hours. Hereupon the double

phosphate of magnesia and ammonia is removed by filtration, washed with water containing one-fourth its volume of ammonia, dried, ignited and weighed as pyrophosphate of magnesia, from which the amount of phosphoric acid is computed.

The sum of the three ingredients must be nearly equal in weight to the amount of the precipitate by the ammonia used in the investigation. These are then computed in reference to the original quantity of the latter.

D.—If the iron ore contains sulphuric acid, a special analysis will be required for its determination. The fine powder is digested with hydrochloric acid, diluted and filtered; to the filtrate chloride of barium is added. The precipitated sulphate of baryta is washed with hot water containing at the beginning a little hydrochloric acid; it is then dried, ignited and weighed.

E.—The amount of the protoxide of iron present is determined by boiling the fine powder with hydrochloric acid, taking care to exclude the air. The solution is then mixed with a large quantity of water and then submitted to the volumetric analysis with permanganate of potassa. If such an ore contains the oxide of manganese, too small a quantity of the protoxide of iron will be indicated, and if the amount of the manganese is so large as to give rise to the evolution of chlorine when treated with hydrochloric acid, there will, naturally, be no protoxide of iron in the solution.

4. MAGNETIC IRON ORE---MAGNETITE.

(SCALES OF IRON FROM THE FORGE.)

The combinations or mixtures of the sesquioxide and protoxide of iron are examined either with the aid of the volumetric methods or alone afterwards.

In the first case the fine powder is heated in a flask with hydrochloric acid. If there is a residue, it consists of foreign admixtures (rocky materials, &c.). The mixture is diluted and filtered. The residue is thoroughly washed and its

weight is determined. The solution is completely oxidized by heating it with a little chlorate of potassa until chlorine begins to be manifest by the smell; the iron is then precipitated by means of ammonia, it is afterwards removed by filtration, washed with hot water, dried and ignited.—A fresh quantity of the substance is dissolved in hydrochloric acid, taking care to exclude all access of air; and the quantity of protoxide of iron is determined by permanganate of potassa by the volumetric method. The mode of computing it will be found, page 63.

In the second case the process is exactly the same as the one given, page 64 1. B.

5. ANALYSIS OF THE OXIDE OF MANGANESE.

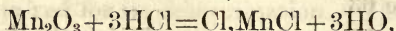
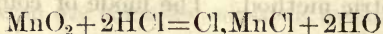
(HAUSMANNITE, PYROLUSITE, BLACK OXIDE OF MANGANESE,
RED OXIDE OF DO.)

Amongst the natural oxides of manganese it is well known, that pyrolusite (polianite) is the richest in oxygen, it is the binoxide of manganese, the so-called black oxide of manganese. Nevertheless the black oxide of manganese of commerce is seldom pure pyrolusite; and even the best sorts contain a certain amount of other intermingled ores of manganese, a circumstance occurring in a still higher degree with the inferior sorts. These mixed ores of manganese (psilomelane, manganite, hausmannite, braunite) contain lower degrees of oxidation of manganese, or consist of such, that is, they are always less rich in oxygen than pyrolusite or the normal black oxide of manganese. Now the value of the black oxide of manganese is proportional to the quantity of oxygen over and above that contained in the protoxide, and which is expressed by the equivalents of chlorine evolved by means of this substance.

But the value of black oxide of manganese is naturally diminished also by the admixture of porphyry, quartz, heavy spar, or by calcareous spar, bitter spar (dolomite), red oxide and brown oxide of iron, in the first place especially on account of the smaller amount of the binoxide of manganese:

and, secondly, if calcareous spar, bitter spar, that is, the carbonate of lime and magnesia, or the oxides of iron are present, owing to the greater expense for the acids required in the preparation of chlorine from such specimens of the black oxide.

Strictly speaking, the value of the oxides of manganese must be computed in reference to the quantity of acid required to produce a given quantity of chlorine. The two formulas stand as follows:

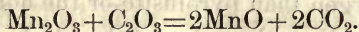
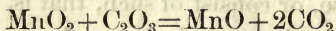


and show, that a specimen of black oxide of manganese, containing only the protoxide, will require one time and a half as much acid for the production of a given quantity of chlorine, as a mineral consisting of the binoxide. Upon the whole, however, this difference is scarcely taken into consideration.

The numerous analyses of the oxides of manganese, already known, all aim to determine the amount of available oxygen either alone or its equivalent in the form of chlorine, carbonic acid, &c. They are partly volumetric analyses, and partly analyses by weight. We give below the best.

A. ANALYSIS BY WEIGHT.

Oxalic acid, C_2O_3 , is converted by the higher oxides of manganese, into carbonic acid, whereby these are reduced into the state of protoxides.



Since MnO_2 is equivalent to $\text{MnO} + \text{O}$ and Mn_2O_3 to $2\text{MnO} + \text{O}$, each atom of oxygen (8 at. wt.) will give rise to the evolution of two atoms of carbonic acid (44 at. wt.), that is, one part of oxygen corresponds to five parts and one half of carbonic acid, or one part of carbonic acid to 0.1818 of oxygen.

From one to two grammes of finely powdered black oxide of manganese are placed in the flask of a Geisler's carbonic acid apparatus, to this are added about two and a half times its amount of simple oxalate of potassa and a little water; the

upper part of the apparatus is then filled with concentrated sulphuric acid and adjusted in its place; the whole apparatus is now accurately weighed in a proper balance. Sulphuric acid is now allowed to flow drop by drop into the flask so that the carbonic acid may be evolved quietly and uniformly until the black color of the oxide has disappeared. A gentle heat is now applied, the carbonic acid in the apparatus is displaced with air and the loss of weight is determined.

One part of carbonic acid = 0.1818 of oxygen,
= 0.8068 of chlorine.

B. Volumetric ANALYSIS.

a) BUNSEN'S ANALYSIS.

This method is applicable not alone for technical purposes but also for the most scientific investigations. It has been described, page 45.

From 0.1 to 0.5 grammes of finely powdered black oxide of manganese are placed in a flask, which is two-thirds full of tolerably concentrated hydrochloric acid; the chlorine evolved is made to pass through a solution of iodide of potassium; each equivalent of which liberates an equivalent of iodine, the amount of which is computed exactly as indicated in the analysis referred to.

Since the equivalents of iodine and chlorine are in the ratio of 127 : 35.5 or of 1 : 0.28, and the equivalents of iodine and oxygen as 127 : 8 or of 1 : 0.063; therefore for each part of iodine indicated by the analysis, 0.28 parts of chlorine or 0.063 parts of oxygen must be computed. (One part of oxygen = 15.875 parts of iodine; and one part of pure MnO_2 = 0.372 parts of oxygen = 5.9055 parts of iodine. On this account an excess of black oxide of manganese is not required.)

b) ANALYSIS WITH PERMANGANATE OF POTASSA.

Ten grammes of pure, dried, crystallized double sulphate of iron and ammonia are dissolved in water, to this the weighed (about 0.5 gm.), finely powdered black oxide of manganese

is added, together with a little hydrochloric acid; a gentle heat is applied so that the oxide is dissolved without setting chlorine free. The solution is then poured into a large quantity of water, which is next placed beneath the burette containing permanganate of potassa, in order to determine the quantity of protoxide of iron not used for oxidation.

Since in this process each atom of oxygen (8) in the oxide of manganese, which is set free, converts 2 atoms of the protoxide of iron into the sesquioxide, it requires also 2 atoms of the double salt, whose equivalent is seven times that of iron, that is, 196, consequently 2 equivalents=392. Since

$$8 : 392 :: 1 : 49$$

one part of oxygen (=4.4375 parts of chlorine) requires precisely 49 parts of the salt which is to be oxidized.

If 0.5 gram: of binoxide of manganese had been taken in the experiment, this quantity containing 0.186 of disposable oxygen, consequently 9.114 grms: of the salt would be used; by the permanganate solution, therefore, 0.886 of the salt (=0.12657 of the iron) would be indicated. If the strength of the permanganate solution is made in reference to metallic iron, the amount of iron indicated by the number of centimetres used, has to be multiplied by 7, in order to determine the corresponding amount of the salt. This is deducted from the quantity started with; the difference(=d) is the oxidized portion, the one-forty-ninth part of which is equal to the quantity of oxygen used.

In order to compute the amount of chlorine, which is to serve as standard for the goodness of the oxide of manganese, the quantity of oxygen found has to be multiplied only by 4.4875 (the ratio of the equivalents of oxygen and chlorine being as 1 to 4.4375).

TESTING FOR MOISTURE.

The powdered mineral is dried in the drying apparatus at a temperature of from 130°F. to 248°F.

6. PSILOMELANE.

We select psilomelane as an example for the complete analysis of an ore of manganese, because it either contains or may contain besides manganese and oxygen, also the oxides of iron, copper, nickel, cobalt, as well as baryta, lime and water.

From 5 to 10 grammes are levigated into an impalpable powder and preserved in a stoppered vessel for future use.

A.—One part is dried in the desiccator in order to determine the amount of hygroscopic water; the results are computed in reference to the substance so dried.

B.—About two grammes are dissolved in hydrochloric acid; and the solution is diluted. If there is any residue, it is removed by filtration, and its amount determined; it consists of rocky material, quartz, or feldspar. To the solution dilute sulphuric acid is added; the sulphate of baryta remains on the filter; it is washed, dried, ignited and weighed; from this weight the amount of baryta is computed. To the filtrate hydrosulphuric acid is added; this separates a small quantity of sulphide of copper, which is removed by filtration; it is ignited in a small porcelain crucible and weighed as oxide of copper. Ammonia is now added in excess to the filtrate, and afterwards the proper amount of sulphide of ammonium; the mixture is digested for some time and then set aside to settle; the fluid portion must have a slight yellow tinge. The precipitate contains in addition to the sulphide of manganese also sulphide of nickel and of cobalt. This, in like manner with sulphide of copper, is filtered in a covered filter; it is then washed quickly and without interruption in cold water containing a few drops of sulphide of ammonium; the filtrate is preserved in a dish. The filter is now removed from the funnel, and placed in a beaker glass, water is first added and then hydrochloric acid; the mixture is digested until all smell of hydrosulphuric acid has been driven off, then filtered into a capacious dish. On the filter will be found the undissolved sulphides of nickel and cobalt mixed with sulphur,

these are dried and ignited; and the residue is weighed. It consists of the oxides of cobalt and nickel, whose separation, owing to their small quantity, is of no avail, although it is necessary to show their presence qualitatively. The solution in hydrochloric acid contains the protoxides of manganese and iron. A small quantity of chlorate of potassa is added to the solution which is now heated in order to oxidize the iron; and when this is effected, a small quantity of alcohol is added to remove the free chlorine. The solution is now diluted with much water, and the two metals are separated by carbonate and acetate of soda (vide page 65).

OBSERVATION.—The smaller the quantity of iron in proportion to that of the manganese, by so much the more difficult it is to hit the right quantity of carbonate of soda to be added. Several of the ores of manganese are quite free from iron; in this case it will, of course, not be necessary to add chlorate of potassa and alcohol: the solution is supersaturated in a dish with carbonate of soda and heated to boiling, and the carbonate of the protoxide of manganese is converted by ignition with access of air into the red oxide of manganese ($=\text{MnO} + \text{Mn}_2\text{O}_3$) from which the amount of manganese or of its protoxide may be computed.

The filtrate from the sulphide of manganese is rendered slightly acid with hydrochloric acid and concentrated by evaporation; the sulphate produced is filtered off; the filtrate is next supersaturated with ammonia and reduced with pure oxalic acid. By this operation a small quantity of oxalate of lime is precipitated, which, after standing for some time, is removed by filtration, washed in hot water, dried and heated to an intense heat, whereby it is converted into caustic lime.

The filtrate is evaporated to dryness; and then weighed. It consists of sulphate of lime, which contains a small quantity of sulphate of magnesia (also perhaps a trace of manganese). If it is intended to determine these metals, the mass is treated in a crucible with water and carbonate of soda, the mixture is then raised to boiling, after which the insoluble portion is placed on a small filter. After ignition and weighing, it is allowed to stand in water containing a few drops of nitric acid. The sesquioxide of manganese remains undissolved; from its weight that of the magnesia is deducted, and by computing both of them as sulphates of the protoxide of manganese and of magnesia and deducting their amount from the

entire amount, that of the sulphate of potassa is obtained.

C.—DETERMINATION OF THE AMOUNT OF OXYGEN. In order to ascertain the degree of oxidation of the manganese, or rather, how much oxygen is at the same time combined with protoxide of manganese, proceed as directed in 5. A. or B.

D.—DETERMINATION OF THE AMOUNT OF WATER. A small quantity of the manganese mineral is weighed and put into a retort in connection with a chloride of calcium tube, which is expanded into a globe in front, into whose terminal tube a perforated cork is fixed to receive the neck of the retort, and which has previously been weighed; the retort is now heated to redness, this drives the water forward into the chloride of calcium tube, which, after the termination of the operation, is again weighed.

OBSERVATION. If a mineral of manganese contains a carbonate (calc spar &c.), this must be removed before the analysis by means of acetic acid or very dilute nitric acid, or the amount of carbonic acid must be determined by a special process (vide Carbonates).

7. OXIDES OF LEAD.

The oxides of lead occur chiefly in the form of litharge in an impure condition, as also of minium.

a. ANALYSIS OF LITHARGE.

Litharge is not a pure oxide of lead. It contains in general silicic acid, carbonic acid, oxide of copper and oxide of iron. The examination is as follows:

1. A small quantity of the fine powder is placed in a porcelain crucible and dried in the desiccator at a temperature of boiling water, it is weighed and then ignited; the difference of weight after ignition gives the amount of carbonic acid.

2. Another quantity is also dried and then dissolved in dilute nitric acid; water is added, and the mixture is filtered; the insoluble portion is silicic acid; to the filtrate contained in a dish, a proper quantity of sulphuric acid is added, and the mixture is then evaporated until the fumes of sulphuric acid begin to be evolved, and is then set aside to cool, after which

it is filtered on a weighed filter, that has previously been dried at a temperature of 248°F . The sulphate of lead on the filter is washed in cold water, then dried in the air first, and afterwards in the drying apparatus until its weight remains constant.

A current of hydrosulphuric acid is passed through the filtrate in order to throw down the copper. Its separation and further treatment will be found described, page 51. The fluid portion is evaporated to a small volume and heated with a few drops of nitric acid in order to convert the iron that had been reduced to the state of protoxide again into that of the sesquioxide; the latter is then precipitated with ammonia.

OBSERVATION. Litharge generally contains also traces of silver, which, according to Kersten, exists in the form of oxide and may be removed by repeated digestion with ammonia. The solution thus obtained is neutralized with hydrochloric acid, whereby the silver is thrown down as chloride. Nevertheless the amount of silver in most specimens of litharge is so small, as almost to be lost in the investigation.

The litharge formed at the beginning of the operation, the *scum* so called, generally contains a considerable amount of antimony, probably of antimonious acid, which, when treated with nitric acid, remains behind.

For the mere determination of the amount of copper, the litharge in the state of a fine powder may be digested in a solution of carbonate of ammonia, which dissolves the oxide of copper. The solution is then evaporated to dryness; and, after ignition, the residue is weighed as oxide of copper.

b. ANALYSIS OF MINIMUM.

This analysis is very simple, and consists in simple ignition, by means of which the minimum is reduced to oxide of lead. Other admixtures, which generally are those of the oxide of lead from which it was originally prepared, may be determined by the method given in the preceding article. Besides this, the specimens of commercial minimum always contain a quantity of oxide of lead in an uncombined condition, which may be determined by digesting the minimum in a solution of the neutral acetate of lead; this dissolves the free oxide and gives rise to the subacetate of lead. By washing and drying the remainder, the difference of weight will determine the amount in question.

8. TIN STONE, TIN ORE.

The stannic acid, that is found native, the so-called tin

stone, generally contains a small portion of oxide of iron and silicic acid, and is not acted upon by acids.

A.—The ore is converted into an impalpable powder, and then a mixture of one part of this powder, three parts of dried carbonate of soda and three parts of sulphur well mixed together are placed in a porcelain crucible and melted over a spirit lamp, taking care to cover the crucible. As soon as the crucible is cold, it is placed in a vessel of water which is heated until the contents (the tin as sulphide of tin) dissolves; the iron (and perhaps also one or more of the other electropositive metals) remains behind as the black sulphide, which is removed by filtration, washed, and, after drying in the air, is ignited in order to convert it into the sesquioxide of iron. (If the quantity is somewhat considerable, the sulphide of iron is dissolved in hydrochloric acid, oxidized and precipitated by ammonia). Sulphide of tin in the diluted alkaline solution is thrown down by dilute sulphuric acid (vide page 59).

B.—There is another method of analyzing tin ore, which may be regarded at the same time as an example of assaying, it consists in placing a given weight of the fine powder in a weighed porcelain crucible and then reducing the ore by means of a current of hydrogen; but the heat in this case must be a vivid red and continued for a long time. After the contents are cold, they are weighed (the vessel being filled with hydrogen gas), and the operation is repeated until there is a certainty that the reduction is complete. From the loss of weight the amount of stannic acid may be determined (one equivalent of oxygen being equal to 4.673 parts of stannic acid), when there is no other oxide present, which might be reduced at the same time. Since, however, tin almost always contains the oxide of iron, a part of the loss must be attributed to this; on this account the crucible together with its contents (the reduced tin) is digested in a beaker glass with hydrochloric acid. As soon as the solution is complete, it is diluted, and filtered into a capacious flask. The amount of residue (silicic acid &c.) is then determined. Ammonia is

added in excess to the filtrate, and then a sufficient quantity of sulphide of ammonium containing so much of the flowers of sulphur as to convert the protosulphide of tin into the sulphide, which must dissolve in the sulphide of ammonium. The contents are now digested in a loosely stoppered flask until the black oxide of iron is completely separated from the yellow fluid; they are then filtered in a covered funnel. The residue is washed in water containing a little sulphide of ammonium, then dissolved in hydrochloric acid, oxidized with chlorate of potassa, and finally the sesquioxide of iron is thrown down by ammonia.

If it is desirable to determine the amount of tin right away, it is precipitated as sulphide by dilute sulphuric acid, &c.

If the amount of oxide of iron is known, the weight of the oxygen which it would lose in the reduction (10 parts of the sesquioxide of iron = 3 parts of oxygen) has to be deducted from the whole weight; the difference is the weight of the oxygen of the stannic acid.

It is much easier by this method to determine the amount of silicic acid &c. than by the method given in A., where it is rendered soluble by fusion with carbonate of soda, or has to be sought for in the sulphide of iron (which may also contain some undecomposed substance).

III. SULPHUR METALS.

In general there are two distinct methods for the analysis of sulphur metals: treatment with *aqua regia*, or with *chlorine*. Although in principle they are both the same, they differ in their execution. When sulphurets are treated with nitro-hydrochloric acid, the metals are converted into chlorides, and the sulphur into sulphuric acid; the solution, therefore, contains at the same time metallic chlorides and sulphates. But this complete conversion of sulphur into sulphuric acid can be effected only when its amount is not very great, or when a large quantity of *aqua regia* is employed to

effect the decomposition of the substance and the digestion is continued for a long time. In by far the most numerous cases a part of the sulphur is separated as such, and can in this form be determined; whilst on the other hand the sulphuric acid, that is produced during the operation, is precipitated by a salt of barium, and from the amount of the sulphate of baryta the oxidized sulphur is computed.

This method, however, can not be followed, when one of the metals contained in the substance gives rise to a chloride which is either with difficulty soluble or altogether insoluble in the acid, as, for instance, *silver* and *lead*; for in this case the chloride is then mixed with the separated sulphur. In like manner the method can not be applied when a metal produces in combination with sulphuric acid a compound insoluble in acids, as, for instance *lead*; for in this case, when sulphuret of lead is treated with nitro-hydrochloric acid there is produced by oxidation a mixture of sulphur, sulphate of lead and chloride of lead in the residue.

In all these cases (and it is just these that occur so frequently, from the fact that a large number of the most important minerals and furnace-products may be placed in this category) *dry chlorine gas* is used for the decomposition, as taught by Berzelius. If a sulphide is treated with chlorine, the bases are all converted into chlorides; and since the chlorides of sulphur, of antimony and of arsenic are volatile, they can easily be separated by heat from the non-volatile chlorides of silver, copper, lead &c.

A.—ANALYSIS OF SULPHUR METALS BY AQUA REGIA.

The sulphur compound to be analyzed must be reduced into an impalpable powder, in order to facilitate the decomposition. If this is neglected, the mineral will have frequently to be digested a very long time, and especially this is the case owing to the fact, that the sulphur, as it separates, surrounds the last remaining heavy parts of the powder and protects them from the action of the acid.

It is always most convenient to make these solutions in small flasks.

As a rule the substance is first covered with *concentrated nitric acid*, added drop by drop, in order that the operation may not be too violent, for which reason also it is generally not advisable to use *fuming nitric acid* for this purpose. It is only when the operation begins to cease, that heat is applied, and continued for some time, still the solution must not be made to boil. As soon as red vapors cease to be given off, an equal volume or even double the volume of concentrated hydrochloric acid is added gradually to the mixture; the digestion is continued until the sulphur appears on the surface of the fluid in the form of one compact yellow mass, or of several yellow drops, nevertheless in all this operation a continued boiling must be avoided. Sometimes it happens, that the sulphur remains all the while of a grey color, especially in single places; in this case the fluid is diluted, and the sulphur is allowed to settle completely to the bottom; after which the fluid portion is carefully separated as much as possible by decantation; the sulphur is again digested with aqua regia, but in smaller quantity than before, until its color changes to pure yellow.

It is not advisable to dry the still impure sulphur without this mode of purification, in order to determine its weight, and afterwards to burn it; for the difference in weight does not determine its amount, because by ignition the remaining part of the sulphur compound undergoes a change, a part of its sulphur passing off as sulphuric acid, whilst the remainder represents a mixture of metallic oxides and basic sulphates.

A sulphur compound must never be *first* treated with hydrochloric acid, because this mode of treatment almost always gives rise to the evolution of hydrosulphuric acid, which thus causes a loss of sulphur. This is especially the case with those sulphides, which are decomposed with diluted acids, as, for instance, the sulphides of iron, zinc, manganese, even of nickel and cobalt. With some of these, indeed, as with zinc and

manganese, a quantity of hydrosulphuric acid is evolved, even when nitric acid is employed first; on which account it is well to prepare a mixture of equal volumes of concentrated nitric and hydrochloric acids, and to heat them together until the color changes to yellow, and chlorine begins to be evolved. Similar precautions must be taken in the analysis of the sulphides of the alkalis and the alkaline earths. The removal of the sulphur, that has been separated from the metallic solution, from the fluid after dilution, varies with its coherence. If the sulphur is in the form of one or of several globular shaped pieces, the fluid is carefully decanted, and the residue is washed repeatedly with water, and is then transferred to a very small porcelain crucible, in which it is dried at a gentle heat in the air. If, on the contrary, the sulphur is divided up into very small flocculent pieces, it is collected on a filter, previously dried at a temperature of 212° F., and, as soon as the contents have been dried in the air, they are transferred to the drying apparatus and submitted to a temperature of 212° until, after repeated weighing, the crucible containing the filter and its contents no longer indicates any further loss of weight.

To be quite safe on this score it is well to *ignite* the sulphur, thus obtained, in a small porcelain crucible. It sometimes happens that there is a residue rising from some undecomposed sulphide. The quantity of this must not exceed a few milligrammes up to a centigramme, if the determination of the amount of sulphur is to be tolerably free from error. Its weight is deducted from that of the sulphur. The substance itself is then dissolved in a few drops of nitro-hydrochloric acid, and the solution is added to that already obtained.—It is much more common, however, for the residue, obtained after all the sulphur has been burned off, to consist of quartz, sulphate of baryta &c., in which case its weight has to be deducted from that of the sulphur as also from that of the substance originally started with.

The sulphuric acid in the acid is now precipitated by chlo-

ride of barium, taking care to avoid any great excess of the precipitant. As soon as the fluid has become perfectly clear, it is filtered. There is less fear in this case than in others that the filtrate will be turbid (vide the section on the Sulphates). The sulphate of baryta is thoroughly washed in hot water and, after drying, it is ignited and weighed.

Since the fluid in general contains nitric acid, especially when the compound was one of those, that are not easily decomposed, and on this account required a greater excess of acid, it happens, that a small quantity of nitrate of baryta is precipitated together with the sulphate of baryta, and is not easily thoroughly removed even by continued washing in hot water; nor even is it removed, when the precipitate, after separation by filtration, is digested for some time in a beaker glass with hydrochloric acid.

The amount of barytic salt adhering is indeed so slight as in many instances to be neglected; but in very accurate investigations this amount must be taken into consideration. In this case the sulphate of baryta, after ignition in the crucible, is covered with concentrated hydrochloric acid; the crucible is then covered and heated to boiling; the contents are diluted with water and submitted to filtration, after which the residue on the filter is thoroughly washed in hot water. It will be always observed in such instances, that the filtrate becomes turbid on the addition of sulphuric acid, owing to the fact, that by ignition the nitrate of baryta had been converted into caustic baryta and carbonate of baryta, which combine with effervescence with this acid.

The metallic sulphides, especially those, that easily evolve hydrosulphuric acid when treated with acids, may be operated upon in the following manner: pulverized *chlorate of potassa* is added to the fine powder in a long necked flask, to which small quantities of *hydrochloric acid* are gradually poured. The flask is set aside for twenty-four hours and afterwards placed in the digester and heated at a temperature of between 86° and 104° F. By this proceeding, as a rule, the

whole amount of the sulphur is dissolved and converted into sulphuric acid. Water is now added, and the mixture is heated, until the whole amount of chlorate of potassa is decomposed, which is shown to be effected when the addition of more acid no longer evolves the smell of chlorine. When this is the case the sulphuric acid is precipitated with chloride of barium.

Now before the separation and determination of the metals can be effected, the *excess of baryta* contained in the fluid must be removed by the gradual addition of dilute sulphuric acid, taking care also here to avoid a large excess. The filtration can take place in this instance before the fluid has become quite clear, as soon as there is a certainty of having added a sufficient quantity of sulphuric acid, because there is no fear of turbidity caused by the particles of the precipitate passing through the fibres.

We will now proceed to a few of the more frequently occurring examples, to which the preceding described operations are supposed to have been applied.

1. SULPHUR AND IRON.

(IRON PYRITES, SPEAR PYRITES, MAGNETIC PYRITES.)

The iron is precipitated by means of ammonia. As regards the determination of the sulphur, and the precipitation of the sesquioxide of iron by means of ammonia, all this has already been given in detail, it will, therefore, be unnecessary to repeat the processes here.

2. SULPHUR, COPPER, IRON.

(COPPER PYRITES, VARIEGATED COPPER, MOST OF THE SPECIMENS OF COPPER GLANCE, AND SEVERAL COPPER ORES.)

A current of hydrosulphuric acid is passed through the acid solution, with all the precautions indicated in reference to the separation of copper and zinc (vide page 51).

The precipitated sulphide of copper is converted into the

disulphide (vide page 52).

The filtrate from the sulphide of copper is so far evaporated in a dish, until the iron is again oxidized by the nitric acid still remaining, or, if this be not the case, by the addition of a few drops of nitric acid or of chlorate of potassa.

The contents are then placed in a beaker glass, to which ammonia is added in order to precipitate the sesquioxide of iron which, after filtration, is thoroughly washed, dried and ignited.

3. SULPHUR, COPPER, IRON, ZINC.

(SEVERAL VARIETIES OF COPPER ORE.)

The process is exactly the same as in No. 2. The filtrate from the sesquioxide of iron is treated with sulphide of ammonium, and then set aside to settle; it is then submitted to a rapid filtration in a covered funnel; the sulphide of zinc is well washed in several waters, and then placed together with the filter in a beaker glass, and digested with hydrochloric acid until all smell of hydrochloric acid has passed off. The solution is much diluted and filtered into an evaporating dish; the residue is well washed on the filter, supersaturated with carbonate of soda, taking care that there is no loss by effervescence, and finally heated to boiling. The carbonate of zinc is then obtained by filtration, washed in hot water, dried and ignited, whereby it is converted into the oxide of zinc.—The filtrate is then tested with a few drops of sulphide of ammonium to ascertain its perfect freedom from all zinc.

OBSERVATION.—This method is not quite accurate, because, although the oxide of zinc alone is easily soluble in ammonia, a small quantity remains with the oxide of iron. Those cases where greater accuracy is necessary, the separation is effected according to No. 4.

Several copper ores contain small quantities of nickel (cobalt). This is found in the course of the analysis with oxide of zinc and is weighed in mixture with it as oxide. If the quantity of both is large enough to admit of a quantitative separation, they are dissolved in hydrochloric acid and separated according to the instructions given, page 54.

If the copper contains *lead*, the analysis must be effected with chlorine.

4. SULPHUR, ZINC, IRON, CADMIUM.

(ZINC BLENDE.)

In the filtrate from excess of baryta a current of hydrosulphuric acid is passed in order to separate the cadmium. The yellow residue is obtained from the fluid by filtration; the fluid itself is received in a dish and evaporated to dryness.

The sulphide of cadmium on the filter is thoroughly washed; it contains some free sulphur owing to the reduction of the sesquioxide of iron, and is treated exactly in the same way as sulphide of zinc precipitated by sulphide of ammonium. The acid solution is precipitated with carbonate of potassa as indicated, page 60.

The amount of cadmium is generally very trifling in zinc blendes; its determination, therefore, is more simply effected out of the sulphides. The latter is then filtered on a weighed filter, which has recently been dried at a temperature of 248° : it is thoroughly washed, and, the tube of the funnel being closed with a small cork, it is treated with sulphide of ammonium previously heated, and set aside, covered up with a plate of glass for a quarter or half an hour. By this means the sulphur, mechanically mixed up with the solution, is separated and drawn out. The cork is now removed and the fluid is allowed to filter off; the sulphide of cadmium on the filter is well washed, dried in a warm place and afterwards in the drying apparatus, until it no longer undergoes any loss of weight.

The filtrate from the sulphide of cadmium is mixed with a small quantity of sulphuric acid and evaporated until the hydrochloric acid, and especially the nitric acid, has all passed off. By this means the iron, which by the hydrosulphuric acid had been reduced to the state of protoxide, will be again oxidized (towards the end of the operation it may be found necessary to add a little nitric acid to aid in the oxidation).

The residue is now highly diluted and then the oxide of iron is separated from the oxide of zinc by means of carbonate of soda and acetate of soda, as already indicated in reference to oxide of iron and protoxide of manganese (vide page 67).

5. SULPHUR, ANTIMONY, IRON.

(ANTIMONY GLANCE, GRAY ANTIMONY, BERTHIERITE.)

The substance is oxidized in the usual way in a flask by means of nitro-hydrochloric acid, As soon as the separated sulphur appears pure, a small quantity of a solution of tartaric acid, and then water are added; the sulphur is then removed, the quantity of sulphuric acid determined, and the excess of baryta again separated by means of sulphuric acid. The introduction of the tartaric acid is intended to prevent the precipitation of the solution of antimony, which otherwise would take place. In this case the sulphate of baryta has to be filtered off as quickly as possible; it is afterwards thoroughly washed with boiling water, ignited and examined in the manner recommended, page 82.

A continuous current of hydrosulphuric acid is now passed through the solution in order to throw down the antimony, until the fluid has a strong smell of the gas; the solution is then allowed to digest at a gentle heat for some time. The sulphide of antimony is received on a filter, previously dried at a temperature of 248°F. and weighed; it is then washed thoroughly in cold water, dried in the air and finally in the drying apparatus at a temperature of 248°F. to 266°F. until it remains constant.

The amount of antimony is determined according to the method given, page 62.

Or a part of the dried sulphide of antimony is placed in a weighed porcelain crucible, which is then covered and maintained at a temperature of 300°F. to 446°F. until the weight no longer undergoes any change. By this means the excess of sulphur has been volatilized, and pure SbS_3 remains in the crucible.

The fluid filtered from the sulphide of antimony, containing iron, is supersaturated with ammonia and then precipitated with sulphide of ammonium. Since the sulphide of iron, by reason of the presence of tartaric acid, is partly suspended in the fluid in a very fine state of division giving it a green color, it must be digested in the covered vessel in the sand-bath, until the precipitate has thoroughly settled, and the solution is clear and of a yellowish color. The sulphide of iron is then filtered as quickly as possible, taking care to cover the funnel during the filtration, in order to obviate the oxidation of the precipitate when exposed to the air; the residue is washed for only a short time, and is then allowed to dry in the funnel. After this the dry filter is folded together, placed in a porcelain crucible and heated with a small quantity of tartaric acid, which in general still adheres to the paper, until both are carbonized, taking care however to avoid an intense ignition. The mass is now digested in a small flask with a little aqua regia, with which the crucible had been previously washed out. As soon as the solution is effected, it is diluted, and then filtered in order to remove the charred residue; after which the sesquioxide of iron is precipitated with ammonia.

OBSERVATION 1.—If a compound of this kind contains at the same time zinc and manganese, these metals are precipitated, together with the iron as sulphides. In this case the process is the same as in the preceding example, dissolving the sulphides in nitro-hydrochloric acid, and evaporating the solution together with sulphuric acid, and so on. Thus, by means of carbonate of soda, a mixture of carbonate of zinc and carbonate of the protoxide of manganese is obtained, which is then dissolved in an excess of acetic acid; from this solution the zinc is precipitated by hydrosulphuric acid. The sulphide of zinc is treated as indicated, page 54; and carbonate of soda throws down the manganese from the filtrate, after all traces of hydrosulphuric acid have been removed.

OBSERVATION 2.—Native sulphide of antimony generally contains sulphide of lead. In this case an accurate determination can be attained only by analysis with chlorine.

B.—ANALYSIS OF METALLIC SULPHIDES BY CHLORINE.

We are indebted to Berzelius for this excellent process, which finds an application not only when combinations of metallic sulphides containing lead or silver, but also when arsenic and antimony are to be analyzed. It requires, however, attention and foresight.

The requisite apparatus consists in the first place of a capacious flask containing a mixture of two parts of black oxide of manganese, three parts of common salt and dilute sulphuric acid (from one and one-half to two parts of water to one of acid). The success of the analysis depends upon the uniform evolution of gas, and this on the proper dilution of the acid. If the latter is too concentrated, the mixture becomes very frothy and is apt to foam over, and at all events produces such a boisterous evolution of gas as to cause a part of the volatile chloride to be lost. If, on the other hand, the mixture is too dilute, the current of gas is too slow and the fluids in the adjoining two-necked bottle are apt to rush back; to obviate which the mixture in the flask has to be heated so intensely as to cause hydrochloric acid to be evolved at the same time with the chlorine. The mixture must be so constituted as to generate, without the application of heat, a regular current of gas for one or several hours, the bubbles of gas passing through the fluid in the first bottle at the rate of one per second, and with the slightest addition of heat much more rapidly.

A cork is accurately fitted to the neck of the flask through which passes the shorter leg of a tube bent twice at right angles; the longer leg passes through a cork in one of the apertures of a two necked bottle and dips down into a layer of concentrated sulphuric acid at the bottom; this acid shows the rate at which the gas is being evolved and also partially dries it. Another tube, bent at right angles at the top and once at the bottom, passes just through the cork in the second neck of the Wolfe's bottle and at the bottom enters the cork of a chloride of calcium apparatus. The gas, after it leaves this vessel, enters the bulb-tube which contains the compound to be analyzed. The bulb-tube is made of glass which does not fuse at a very low temperature. The bulb is capacious enough for the material to be analyzed, the tube at one side is wider and longer than the other. The bulb-tube is first weighed, and then from one to two grammes of the impalpable powder

to be analyzed are introduced through the wider tube into the bulb. The tube is now cleaned with a feather and then the whole is weighed. The narrow and shorter tube is connected with the chloride of calcium apparatus; the longer tube is bent at right angles and connected with a Liebig's potassa apparatus of rather large dimensions, but its legs must be parallel. This vessel is filled with dilute hydrochloric acid, to which tartaric acid is added when the mineral contains antimony. A tube proceeds from the second leg of this vessel through a cork in a two-necked bottle and dips into a similar solution at the bottom of the bottle from which another conducts the chlorine away out of the laboratory.

As soon as all the the connections are accurately made, chlorine gas is evolved and a current is kept up for one or several hours. Gradually the apparatus becomes filled with chlorine; in general the temperature of the substance rises considerably owing to the decomposition effected; and white vapors appear in the tube and first receiver. The evolution of gas can be so great as to cause the first two-necked bottle to be filled with vapor, and a small portion may pass into the last; but this latter event must be avoided, otherwise a part might easily escape into the air.

The bulb of the bulb-tube is heated with an ordinary small spirit lamp taking care not to commence this operation before all the parts are filled with chlorine. But at this point the greatest attention is required in reference to the evolution of gas; for it can easily happen to the inexperienced, that the fluid can be drawn over out of the first bottle into the flask, or that by a sudden formation of aqueous vapor a part of the volatile chloride may pass without absorption through the receivers. All this is a matter of experience to know how to avoid such mishaps; for, when the flask is heated, the gas is quickly absorbed and thus by condensation the fluid may rush backwards; and the application of a higher temperature in order to prevent this misadventure easily causes too much vapor to rise, which is carried along with the gas. The aim is

always to generate the gas so that the bubbles are perceived in the two receivers at considerable intervals of time between them.

The volatile chlorides, that collect in the first branches of the bulb-tube, are driven forwards by means of a small spirit lamp, taking care that the tube does not get stopped up during the operation, a circumstance that easily occurs unless the bore of the tube is pretty large. If after continuous heating of the bulb, (and this heat must never rise so high as a visible red heat, because it might easily happen that a part of the chlorides of lead, copper &c. might be volatilized) there is no longer any deposit in the adjacent parts of the tube (if the substances contain iron, the chloride of iron will be continually formed and this is not so easily volatilized, and its complete volatilization is not to be expected), and the sublimate has been driven forward by means of the blowpipe as far as the cork of the receiver, the tube is scratched with a sharp file a little distance above the cork and there broken off by means of a point of burning charcoal. The aperture of the piece remaining in the cork, however, must be closed immediately with a small cork held in readiness for this purpose.

The chloride of sulphur, that has arrived as far as the water in the receiver, is decomposed by giving rise to hydrochloric acid, sulphur and sulphurous acid which by the free chlorine is converted into sulphuric acid. It frequently happens also, that the whole amount of sulphur is dissolved as sulphuric acid.

After the termination of the experiments the two bottles are set aside for about 24 hours, in order that the chlorides, that remain in the broken tube, may dissolve. If this does not take place of itself, the small cork is removed from the tube, the tube itself also is drawn out of the larger cork, and then, letting it drop into the receiver, the aperture is immediately closed with a large cork held in readiness, in order that none of the very volatile vapors may escape. After the time

above-mentioned the contents of the receivers are poured into a beaker glass, the receivers themselves are well rinsed with water, and the combined fluids are digested at a gentle temperature, until the smell of chlorine has passed off. If there is any free sulphur present, it is placed on a weighed filter, if not, the sulphuric acid is precipitated with chloride of barium; the sulphate of baryta thus produced is well washed in hot water, and after ignition, if the fluid contain tartaric acid, it is treated as indicated, page 83, after which the excess of baryta is removed by dilute sulphuric acid.

These operations are the same in all analyses of this kind; the remaining operations in reference to the separation and determination of the metals will be given in detail in the following examples, in which the further treatment of the contents is described under A. and that of the volatile chlorides under B.

1. SULPHUR, ANTIMONY, SILVER.

(RUBY SILVER, BRITTLE SILVER ORE, MIARGYRITE.)

These compounds are the most easily decomposed of all others.

A.—Since the bulb in this case contains only chloride of silver, all that is necessary after the termination of the operation is to weigh the bulb-tube together with the piece that has been cut off, as soon as they have been thoroughly dried, in order to ascertain the amount of chloride of silver.

B.—The antimony is precipitated by hydrosulphuric acid; the further process is the same as indicated on page 62.

OBSERVATION.—If the substance contains small amounts of copper and iron, the mode of proceeding is that given (Grey Copper) on the next page.

2. SULPHUR, ANTIMONY, LEAD.

(ZINKENITE, PLAGIONITE, JAMESONITE, BOULANGERITE, FEARER ORE.)

The analysis is exactly the same as in 1. The bulb-tube is weighed with the chloride of lead.

If there are traces of copper and iron present, the contents of the bulb are treated with a few drops of hydrochloric acid and hot water, with the aim of removing them from the glass; they are then poured into a dish and heated to boiling, afterwards filtered on a weighed filter whilst still hot; and the filtrate is received in a second dish containing dilute sulphuric acid. The residue is boiled repeatedly with water slightly acidulated, as long as chloride of lead is dissolved, it is then thoroughly washed in hot water on the filter; and its weight is determined. It may consist of undecomposed matter, rocky substance, or chloride of silver, which must be examined more intimately. The filtrate is evaporated to dryness, the lead is determined as sulphate of lead (vide page 55.); the filtrate is then precipitated by hydrosulphuric acid; the small quantity of sulphide of copper is ignited, computed as oxide, and finally the filtrate, containing still a small portion of iron, is added to that from the sulphide of antimony.

As soon as the antimony has been precipitated by hydrosulphuric acid, the fluid is supersaturated with ammonia, and then sulphide of ammonium is added. The sulphide of iron having been completely separated by continued digestion, is removed by filtration, raised to a low red heat, dissolved in aqua regia, and precipitated by ammonia as oxide of iron. (Compare page 87).

3. SULPHUR, ANTIMONY, LEAD, COPPER, IRON.

(BOURNONITE.)

The analysis of this material is the same as in the preceding example. The amount of copper, however, being somewhat considerable, the sulphide precipitated by hydrosulphuric acid is converted into the disulphide of copper, as indicated, page 53.

4. SULPHUR, ANTIMONY, ARSENIC, COPPER, IRON, ZINC.

(GREY COPPER.)

Chloride of silver, chloride of copper and the largest parts of the chlorides of iron and zinc will be found in the bulb of the bulb-tube. The chlorides of sulphur, of antimony, of arsenic, as well as a part of the chlorides of iron and zinc are volatilized.

A.—*Analysis of the Non-volatile Chlorides.* The contents of the bulb are transferred by the aid of a little hydrochloric acid and water to a beaker glass, the chloride of silver is then placed in a weighed filter, and the copper is precipitated by hydrosulphuric acid, as indicated, page 52. The filtrate from the sulphide of copper is evaporated in a dish to a small amount, and afterwards added to the solution to be obtained from the remaining part of the iron and zinc by the B analysis.

B.—*Analysis of the Volatile Chlorides.* As soon as the sulphuric acid is precipitated by chloride of barium, and the excess of baryta has been removed again by sulphuric acid, according to processes already given, a current of hydrosulphuric acid is passed through the fluid for some time, in order to precipitate antimony and arsenic at the same time. Since arsenic is thrown down later than antimony and only slowly, the current has to be continued longer, and when the fluid exhales a strong smell of the gas, it is heated on a sand-bath for some time, it is then allowed to cool and afterwards filtered, after which the two sulphides are thoroughly washed in cold water. The filtrate may again be treated with hydrosulphuric acid, and afterwards heated in order to ascertain whether any more sulphide of arsenic can be obtained. If this should be the case, the small quantity of sulphide of arsenic has to be placed on a separate filter, which is then dried and weighed; from this the amount of arsenic is computed, taking it for granted that the arsenic exists here as AsS_3 , which may be regarded without hesitation for so small a quantity to be the case.

The mixture of sulphide of antimony and sulphide of arsenic, previously dried in the air, is placed together with the

filter in a flask; here it is oxidized either by means of aqua regia, or chlorate of potassa and hydrochloric acid. If the sulphur has thoroughly separated, a small quantity of tartaric acid is added, then water, and the fluid is filtered. A considerable quantity of chloride of ammonium is added to the filtrate, which is neutralized with ammonia in excess, the fluid remaining clear all the while; the magnesia mixture (vide page 67) is now added which precipitates the arsenic acid as the double arsenate of ammonia and magnesia. The mixture is now set aside in a cool place to settle, after which the residue is placed on a dried and weighed filter, and washed with cold water to which one quarter of its volume of ammonia has been added. After drying in the air, it is dried at a temperature of boiling water until its weight remains constant. It is then represented by the symbol: $2 \text{MgO} + \text{NH}_4\text{O} + \text{As}_2 + \text{Aq}$.

The filtrate is now neutralized with hydrochloric acid in excess; and the antimony is precipitated by hydrosulphuric acid and treated as sulphide of antimony (vide page 62).

The filtrate from the sulphide of antimony and sulphide of arsenic is supersaturated with ammonia and then precipitated with sulphide of ammonium. As soon as the iron and zinc have been precipitated, and by digesting with heat have thoroughly settled from the yellowish fluid, they are placed in a covered filter and washed as quickly as possible with cold water, to which a few drops of sulphide of ammonium are added every time fresh water is used. The filter is now placed in a beaker glass, covered with hydrochloric acid and digested in the sand-bath, until all is dissolved, and all smell of hydrosulphuric acid has passed off. The solution is slightly diluted with water then filtered and added to the filtrate obtained from A. The iron is now oxidized by means of a little chlorate of potassa and then separated from the zinc according to the process given on page 67.

5. SULPHUR, LEAD, IRON, COPPER, SILVER, ZINC, NICKEL, ANTIMONY.

(LEAD STONE, LEAD AND COPPER STONE.)

Furnace products of this kind contain of metals either lead and iron (lead stone) or copper, lead and iron (copper and lead stone). The remaining metals exist in these products to a very small extent.

The decomposition of such electro-positive sulphides by means of chlorine is much slower than that of the preceding compounds; the process is given in the 2nd and 3rd examples; the non-volatile chlorides contain lead, copper, a part of the iron, and zinc. The volatile chlorides in the receivers (no tartaric acid need be added to the fluid) are treated with hydrosulphuric acid as soon as the sulphur has been separated, as also the sulphate of baryta and the excess of the chloride of barium; this treatment precipitates a small quantity of antimony; the filtrate from this is combined with that obtained from the sulphide of copper, and serves to determine the amount of iron and zinc, the latter of which sometimes contains nickel.

IV. ARSENICAL METALS and their Sulphides.

Of the compounds of arsenic with metals those of iron, nickel, and cobalt are in general of the most frequent occurrence, and their analysis is of most importance.

There are several methods of analyzing these compounds; the best mode of proceeding, however, is to oxidize them with aqua regia, thus giving rise to arsenates of metallic oxides, and then to decompose these at a red heat with carbonate of soda, or to precipitate the arsenic with hydrosulphuric acid.

1. ARSENIC AND IRON.

(LEUCOPYRITE.)

The substance is first reduced to an impalpable powder

and then covered in a flask with concentrated nitric acid; as soon as the violence of the action has ceased, the contents are digested for some time, then mixed with hydrochloric acid and heated until the solution is effected (quartz &c. being left undissolved). Or the substance is oxidized with chlorate of potassa and hydrochloric acid, and maintained at a gentle heat, until all is dissolved; afterwards it is diluted with water and heated in an evaporating dish as long as there is any smell of chlorine.

If it were desirous to treat the solution directly with hydrosulphuric acid in order to separate the arsenic, the separation would proceed very slowly, because arsenic is precipitated quite gradually, and a fluid, containing arsenic acid and thoroughly saturated with hydrosulphuric acid, can still retain in solution much of this metal; and a continuous current of gas even for several days, digesting in heat, and repeated filtration would be required to effect the object in view. It is much easier, however, to precipitate solutions containing arsenious acid; in consequence of this, as was first proposed by Woehler, arsenic acid is reduced to arsenious acid, and then precipitated with hydrosulphuric acid. This reduction is best effected with sulphurous acid. But since free nitric acid, on account of its oxidizing properties, is antagonistic to this reduction, it must be removed from the solution.

The solution, therefore, of arsenical iron is placed in a dish and evaporated to a small volume, adding towards the last a small quantity of hydrochloric acid; it is then diluted with water and so much acid sulphite (potassa, soda) is added, until it has a strong smell of sulphurous acid, but still has an acid reaction. It is then set aside for several hours, after which it is heated to drive off this smell, and placed in a beaker glass; a current of hydrosulphuric acid is now caused to pass through the solution for some time.

An aqueous solution of sulphurous acid may also be used instead of the alkaline sulphite, or the gas itself may be made to pass through the fluid. On account of the injurious action

of nitric acid, as a reducer, it is frequently preferable to dissolve the arsenical mineral by means of chlorate of potassa and hydrochloric acid. Hydrosulphuric acid is then passed through the fluid until the latter has a strong smell of this gas; it is then set aside uncovered in a gentle heat until the smell has ceased; the sulphide of arsenic is then removed by filtration. The gas is again passed through the filtrate, which is also heated as before, in order to ascertain whether any arsenic still remains in the solution. The precipitate is washed with cold water; it is then dried in air and oxidized either by means of aqua regia, or chlorate of potassa and hydrochloric acid, from which the amount of arsenic may be computed in the form of the double arsenate of ammonia and magnesia by the method described, page 94.

There now remains still the fluid containing iron, filtered from the sulphide of arsenic. This filtrate is evaporated in the dish to a small bulk, oxidized with nitric acid, diluted, poured into a beaker glass and precipitated with ammonia. From the amount of precipitated sesquioxide of iron, after a thorough washing, drying and ignition, the amount of iron may be computed.

OBSERVATION 1.—Arsenical iron ore generally contains a small quantity of sulphur. In this case it is best to use a fresh quantity and oxidize it in like manner with nitrohydrochloric acid, and then precipitate the diluted solution with chloride of barium.

OBSERVATION 2.—If the arsenical iron ore contains so much nickel or cobalt as to make it necessary to determine its amount, their separation from the iron is effected by the method described in the following examples.

The following is a second method of analysis: a given quantity of the substance, reduced to an impalpable powder, is mixed in a porcelain crucible with three times its weight of dried carbonate of soda, as also three times its weight of sulphur. The crucible is then covered, and the mixture is melted over the lamp. In this experiment the crucible is not attacked. As soon as the crucible is cold, it is immersed in water, which is then heated to effect a solution. The sulphide of iron is then filtered from the solution containing sulpharsenide of sodium. The latter is concentrated by evaporation, placed in a flask, and carefully supersaturated with hydrochloric

ric acid to which chlorate of potassa is gradually added in order to oxidize the separated sulphide of arsenic, the process being the same as that given before, page 94. After the addition of chloride of ammonium the arsenic is precipitated as the double arsenate of ammonia and magnesia.

The sulphide of iron is dissolved in hydrochloric acid, oxidized by a small quantity of chlorate of potassa, and the sesquioxide of iron is precipitated by ammonia.

It is still a simpler method to heat the solution of the arsenical iron ore in nitro-hydrochloric acid (or in chlorate of potassa and hydrochloric acid) with an excess of the hydrate of potassa to boiling. By this means the sesquioxide of iron is separated, which is then removed by filtration, thoroughly washed, dissolved in hydrochloric acid, and again precipitated by ammonia. The alkaline fluid is made acid with the same acid, excess of ammonia is then added, and finally arsenic acid is precipitated in the form of the double arsenate of ammonia and magnesia. (Nevertheless arsenic acid can be separated in this manner from no other oxides except those of iron and copper.)

If it is required to determine the amount of iron alone in any arsenical iron ore, the fine powder is mixed in a porcelain crucible with sulphur and then ignited with hydrogen gas. This experiment is repeated. The proto-sulphide of iron, Fe S , then remains.

2. SULPHUR, ARSENIC, IRON.

(MISPICKEL, ARSENICAL IRON).

The analysis of such a compound, in which the sulphur forms an essential component, is made in the same manner as that of arsenical iron. It is dissolved in nitro-hydrochloric acid, or in hydrochloric acid and chlorate of potassa; the amount of separated sulphur, as well as the amount of sulphuric acid that has been produced, is determined in the manner indicated on page 79 for the metallic sulphides; the excess of barryta is removed, and the iron is separated from the arsenic;

or a separate quantity of the substance may be devoted to the special determination of sulphur itself.

The amount of iron also may be determined by heating the substance, mixed with sulphur, in hydrogen gas (vide above).

3. ARSENIC, NICKEL, COBALT, IRON, COPPER, ANTIMONY.

(COPPER NICKEL, WHITE NICKEL, SMALTINE, NICKEL GLANCE, COBALT GLANCE, COMMERCIAL NICKEL.)

These substances differ only in respect to the quantities of their components. In copper nickel and white nickel, in nickel and cobalt glance, and in nickel the latter predominates, and this is the case in several specimens of smaltine; whilst in the other forms the amount of cobalt is very nearly equal to that of nickel or even exceeds it. Iron is always or almost always present. Arsenic, as well as iron (and copper) exists in exceedingly small quantities in commercial nickel.

In the following table will be seen at a glance the amounts of these components in such substances, as determined by the analyses up to the present time:

	Arsenic.	Nickel.	Cobalt.	Iron.
Copper nickel	50—56	40—45	0.1—0.3	0—2.7
White nickel	70—72	21—30	0—4	0—13
Smaltine	50—80	0—35	3—24	1—19
Glances (speise)	26—44	5—55	0—23	0—10
Nickel (commercial)	0—5	75—90		3—6

Nickel and cobalt are probably always found in these ores; and if in the analyses, that have hitherto been made, only one of them is reported as found, it is probable that the other also is present in very small quantity, but has been overlooked.

1. *Method.*—The compound, as in No 1., is reduced to an impalpable powder and then oxidized either by means of nitro-hydrochloric acid, or by chlorate of potassa and hydrochloric acid; and the arsenic is precipitated and determined by the method indicated.

The filtrate from the sulphide of arsenic is heated in order to get rid of all hydrosulphuric acid. The iron is then oxidized by means of chlorate of potassa; the chlorine is expelled by the application of heat and the addition of a little alcohol; the fluid, highly diluted, is placed in a dish and mixed with carbonate of soda, so that a little oxide of iron (as a basic salt) begins to separate, but a part of the iron remains still in solution, or at least so far, until the fluid, in consequence of the formation of a basic salt of the sesquioxide of iron, assumes a dark red brown color; it is then mixed with acetate of soda and heated to boiling (vide page 67). By this proceeding the iron is wholly precipitated as a basic salt of the oxide, whilst the oxides of nickel and cobalt remain in solution; and the fluid, according as either one or the other predominates, assumes either a greenish or a light red color. The precipitate of iron is filtered hot, thoroughly washed with hot water, and then again placed in the dish together with the filter; here it is dissolved in dilute hydrochloric acid, and, after filtration, the iron is thrown down as the sesquioxide by means of ammonia. (No precipitate must be produced, nor any discoloration by the addition of sulphide of ammonium.)

To the filtrate, in a dish containing nickel and cobalt, hydrate of potassa is added in excess, it is then heated to boiling, filtered and washed whilst hot. The mixture of the two oxides is then dissolved in acetic acid. A concentrated solution of nitrite of soda (if it contains any free potassa, you must see that there is an excess of acetic acid) is added to this solution, and then the mixture is set aside for twenty-four hours. By this means a yellow precipitate is formed of the double nitrite of the sesquioxide of cobalt and potassa; this is removed by filtration and thoroughly washed by a saturated cold solution of chloride of potassium. Nitrite of potassa is again added to the filtrate, which is allowed to stand for a long time, in order to be certain that there is no longer any more precipitate formed. The yellow precipitate is now

digested with hydrochloric acid with which it is dissolved by the evolution of chlorine; the fluid is next diluted and filtered into a dish; and the oxide of cobalt is precipitated by boiling with an excess of hydrate of potassa. The precipitate is thoroughly washed whilst hot, then dried and strongly ignited in a porcelain crucible in hydrogen gas, by means of which cobalt is reduced to the metallic form. After cooling in a current of the gas it is weighed in the covered crucible. Since this is very difficult, however, to remove every trace of potassa from the oxide of cobalt by washing, the reduced metal (if the analysis is to be quite accurate) must be washed with water and then again ignited in hydrogen gas.

The filtrate from the precipitated cobalt contains nickel, which is thrown down by boiling with hydrate of potassa. After careful washing, in order to remove the alkali, drying and igniting, pure oxide of nickel is obtained, from which the amount of nickel may be computed,

The weight of the two metals together may also be determined, the cobalt then precipitated, and the amount of nickel will be the difference of the two weights. In this case the two oxides are dried (the filter is incinerated, and the ashes added thereto) and reduced in hydrogen gas, then weighed; and, when great accuracy is required, the reduced metal is carefully washed, once more ignited in hydrogen gas and again weighed. It is finally dissolved in nitric acid; the solution is diluted and then treated with nitrite of potassa.

2. Method.—The substance is reduced to a very fine powder and then placed in a covered porcelain crucible, mixed with sulphur, and heated to ignition. This operation is repeated once or oftener until no longer sulphide of arsenic volatilizes. By this mode of proceeding all the arsenic, with the exception of a mere trace, is volatilized, and there remains a mixture of metallic sulphides. The volatilization of the arsenic takes place the more slowly the greater the proportion of cobalt contained in the substance, and, on this account this method is adopted neither for cobalt proper (speisekobalt), nor

when the substance contains antimony. The metallic sulphides are dissolved in nitro-hydrochloric acid, or in chlorate of potassa and hydrochloric acid; and the separation of iron, nickel and cobalt is effected by methods already given. The amount of arsenic is represented by the amount of loss.

Several of the substances above-mentioned contain other components, but in very small quantities, besides those already given.

Sulphur is found in almost all of them. To determine its amount it is better to employ a separate quantity of the substance; the process is the same as that in No 2., or according to page 79.

Silica occurs in commercial nickel and is separated by dissolving the latter in nitric acid, &c., as silicic acid, of which, however, a small portion remains in solution. The whole is, therefore, evaporated to dryness on the water bath; the residue, after cooling, is moistened with acid, then treated with water, after which the silicic acid is separated by filtration; the filtrate requires further treatment.

Antimony is found in nickel and cobalt ores, and also in gray nickel. This substance is precipitated together with the arsenic by hydrosulphuric acid, and its separation is effected according to the method given on page 93.

COPPER, BISMUTH, LEAD.—When these metals are present in small quantities, a current of hydrosulphuric acid is passed through the solution a short time. They are thrown down sooner than the arsenic, but always to a small extent accompanied with this metal. The solution is filtered, and then a current of hydrosulphuric acid is passed through the filtrate until the whole of the arsenic has been separated. The precipitated metallic sulphides are placed, while still moist, together with the filter itself in a flask, and digested at a pretty high temperature with concentrated yellow sulphide of ammonium.

After the solution is cool, it is diluted and filtered in a covered funnel; the residual sulphurets are washed well with water mixed with a few drops of sulphide of ammonium; the filtrate is neutralized with a slight excess of hydrochloric acid, and the precipitated sulphide of arsenic is separated by filtration and afterwards added to the principal mass already obtained. The sulphides are separated from each other, if their quantities will permit it, by methods indicated on pages 55 and 56.

If the quantities of such metals are considerable, which is the case with several of the furnace-products designated as mixtures (Speise), their mode of analysis will be given in a subsequent article. (Example 5.)

4. SULPHUR, ARSENIC, ANTIMONY, NICKEL, COBALT, IRON.

(NICKEL GLANCE, COBALT GLANCE, MIXTURES—SPEISE).

The analysis of such substances, as contain a large amount of sulphur, is effected on the whole as in the preceding example. The estimation of all the components is determined either from one and the same amount of substance, that is to say, the sulphur that is set free by the solution is first determined, the sulphuric acid is precipitated by chloride of barium, the excess of baryta is then removed and finally the metals are separated. Or two separate quantities of the substance are employed, one for the determination of the amount of the sulphur, and the other for that of the metals, the process to be used being that given in example 3.*

If arsenic and antimony are both present (several specimens of nickel glance) the determination of both of them is made according to instructions found on page 93.

If small quantities of copper are present, the remarks to be found on page 102 are valid here.

*Nickel glance and mispickel comport themselves with regard to nitric acid like the simple metallic sulphides, the metal is first oxidized, and then the sulphur, a part of the latter being set free. On the contrary cobalt glance dissolves in nitric acid without liberating sulphur.

The method adduced in the preceding example for decomposition by means of sulphur (2.) can be adopted here only in those cases where the substance contains no antimony and but little or no cobalt. Naturally the method in question is intended only for the determination of electropositive metals. According to Rose* all such substances, not containing antimony, may be converted indeed by means of acid sulphate of ammonia into sulphates free from arsenic; but the crucibles will be thereby acted upon.

5. LEAD AND COPPER MIXTURES.

The substances designated by the names Lead-speise and Copper-speise belong to the most complicated compounds, that are found in the furnace-products after the smelting of lead and copper ores containing arsenic and antimony; for these contain copper, lead, iron, nickel, cobalt, zinc, bismuth, silver, arsenic, antimony and sulphur.

A.—*Mixtures containing little or no lead or antimony.*

One part is set aside for the determination of the sulphur; another is dissolved either in nitro-hydrochloric acid, or in hydrochloric acid and chlorate of potassa. The silver generally exists in these mixtures in such a trifling quantity as not to leave any precipitate of chloride of silver. If any chloride of lead has separated, it is again dissolved in boiling water. The solution is then treated with hydrosulphuric acid, which precipitates lead, copper, bismuth, antimony and arsenic as sulphides; these are separated by filtration. Hydrosulphuric acid is again passed through the filtrate, previously heated, in order to be certain that all the arsenic has been completely precipitated. The metallic sulphides are digested with concentrated yellow sulphide of ammonium in order to dissolve the sulphides of antimony and arsenic, adding so much the more of the reagent and continuing the digestion (even to boiling) so much the longer, according to the greatness of the amount (vide page 102). After filtration the

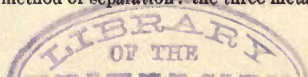
* Poggend. Ann.. Page 466.

two sulphides are precipitated by hydrochloric acid and then separated according to instructions given on page 93.

The undissolved sulphides of copper, lead and bismuth are dried in the air and rubbed off from the filter into the dish; the filter itself is ignited, and the ashes are dissolved alone in a small porcelain crucible in nitric acid. The mixture of sulphides in the dish is also dissolved in nitric acid, from which the impure sulphur is removed, and digested with heat in nitric acid. These three solutions are mixed together. (A small quantity of sulphate of lead may remain undissolved; this is to be collected and weighed on a weighed filter). The solution of the three metals in nitric acid is concentrated by evaporation, and then lead is separated first according to the process given on page 56. From the filtrate the bismuth is next precipitated, and finally the copper (vide page 56).

In the filtrate from the precipitate made by hydrosulphuric acid are found still iron (in the form of protoxide), nickel, cobalt, and zinc. It is evaporated in order to get rid of the hydrosulphuric acid and most of the free acid; the iron is then oxidized by means of a little chlorate of potassa; the fluid is diluted; the free chlorine is liberated by heat and a few drops of alcohol; and finally the sesquioxide of iron is separated from the rest according to the method given, page 66. To the filtrate raised to boiling an excess of carbonate of soda is added; the precipitate is removed by filtration and is dissolved without washing in an excess of acetic acid. A current of hydrosulphuric acid is now passed through the diluted fluid; this precipitates the zinc alone. The sulphide of zinc is filtered off, dissolved in hydrochloric acid, and precipitated as carbonate of zinc by means of carbonate of soda. The filtrate from the sulphide of zinc is concentrated by evaporation; to this is added nitrate of potassa (and, when necessary, free acetic acid) to separate cobalt and nickel (vide page 99).

OBSERVATION.—The separation of zinc from nickel and cobalt by the method described succeeds only in the presence of the requisite amount of free acetic acid. Moreover the precipitation of the sulphide of zinc must not be continued too long, otherwise a small quantity of sulphide of nickel and of sulphide of cobalt will be precipitated at the same time. The following is another method of separation: the three metals



are thrown down as carbonates; these are filtered, washed hot, dried and ignited. The oxides are reduced to an impalpable powder, mixed intimately in a porcelain crucible with an excess of sulphur and then heated in hydrogen gas (vide page 53). The sulphides thus produced are treated in the cold with highly diluted hydrochloric acid, which dissolves the sulphide of zinc alone, and leaves as a residue the sulphides of nickel and cobalt, which are dissolved in nitric acid, after which the two metals are separated.

B.—*Mixtures containing much lead or antimony.*

The substance, previously reduced to an impalpable powder, is decomposed by heat in chlorine, as described on page 88. The decomposition is not effected, as is the case with the metallic sulphides, in the cold; it is only when the substance is heated that the decomposition takes place, and then so suddenly and energetically as to require the greatest caution. The bulb contains, after the termination of the operation, the non-volatile chlorides of lead (silver), bismuth, copper, nickel, cobalt, and partly those of iron and zinc. They are dissolved by treating them with water and hydrochloric acid, leaving as a residue undecomposed material and chloride of silver, which are collected on a weighed filter, and after weighing are separated by ammonia. The solution in hydrochloric acid is filtered into a dilute solution of sulphuric acid and evaporated; lead is then separated as sulphate of oxide of lead, proceeding as indicated on page 55. A current of hydrochloric acid is passed through the fluid; this precipitates copper and bismuth which are separated as indicated on page 56. The filtrate, containing iron, zinc, nickel and cobalt, is treated as above prescribed.

The sulphuric acid is first separated from the volatile chlorides by means of chloride of barium, the excess of baryta being in its turn removed by sulphuric acid, then the antimony and arsenic are thrown down by hydrosulphuric acid and afterwards separated as indicated on page 94. The filtrate contains still iron and zinc, the treatment of which will be found on page 95.

6. ARSENIC, ANTIMONY,

The substance, reduced to a fine powder, is heated in a

bulb-tube in a current of dry carbonic acid. As soon as the whole arrangement is filled with this gas, heat is applied to the substance and continued as long as arsenic is volatilized.

This metal is removed from the tube by applying heat gradually along the tube to the end. In this operation a high temperature must be avoided; and it is well to perform it in a place where there is a good draft of air. By weighing the residual quantity of antimony, the amount of arsenic is determined.

If it be desired to determine both the metals directly, dissolve the substance in aqua regia, or in hydrochloric acid and chlorate of potassa; tartaric acid is then added to the solution, and afterwards chloride of ammonium; the solution is then neutralized with ammonia in excess. The arsenic acid is finally precipitated by salt of magnesia as the double arsenate of ammonia and magnesia, after which the antimony in the filtrate is determined as prescribed on page 94.

7. ARSENIC, TIN.

The alloy is divided up as much as possible, then intimately mixed with five times its weight of carbonate of soda and five of sulphur; the mixture is then melted at a low heat over the lamp. As soon as it begins to flow gently, it is kept ignited for some time. When cool the mass, consisting of the double sulphide of arsenic and sodium and the double sulphide of tin and sodium, is completely dissolved in water (traces of electro-positive metallic sulphides, for instance of iron, copper, lead, remain undissolved); the solution is highly diluted, then hydrochloric acid is added in excess; and the mixture is kept digesting at a very gentle heat, until all smell of hydrosulphuric acid has passed off. The sulphides of tin and arsenic, that have separated, are collected on a weighed filter, washed thoroughly with cold water, containing a few drops of acid, dried in the air, then in the drying apparatus at a temperature of boiling water, until their weight remains constant.

A part of the dried sulphides is placed in a weighed bulb-tube, as already described for the analysis of metallic sulphides by means of chlorine, page 88; the remaining part, together with the filter, is again dried in order to ascertain the quantity in the bulb. The wider tube attached to the bulb is bent at an obtuse angle and dips just below the surface of a quantity of ammonia placed in a two-necked Woulfe's bottle. The narrow tube of the bulb is connected with an arrangement through which dried hydrosulphuric acid is generated and passed. As soon as the whole arrangement is filled with gas, the bulb is heated, as also the wider tube, by which the sulphide of arsenic is driven forward into the ammonia. As soon as there is no longer any formation of the yellow sulphide of arsenic, the bulb is allowed to cool in a current of gas; and the projecting part of the wide tube is broken off, taken out of the cork and digested in warm water in order to wash off all adhering substance; the wash-water is then added to the ammoniacal solution in the Woulfe's bottle. This fluid is next supersaturated in a flask with hydrochloric acid, to which chlorate of potassa is added, in order to oxidize the sulphide of arsenic by digestion at a gentle heat. To the filtrate from the sulphur ammonia is added in excess, which precipitates the arsenic as the double arsenate of ammonia and magnesia.

The sulphide of tin in the bulb, a mixture of protosulphide of tin, SnS , and a small quantity of sulphur, is shaken into a weighed porcelain crucible, moistened with nitric acid, and carefully heated, in order to convert it into stannic acid. (vide page 60).

If arsenic is not to be determined by a direct method, the metallic sulphides are treated with hydrosulphuric acid in a porcelain crucible, in which then the sulphide of tin remains unvolatilized.

V. SULPHATES.

In the analysis of the sulphates the process varies according as they are soluble or insoluble in water or in acids.

Soluble in water are the sulphates of the alkalies, of magnesia, of alumina, and of most of the metallic oxides, if they are neutral.

Soluble in acids are the basic sulphates of alumina and of most of the metallic oxides. Hydrochloric acid is their most appropriate solvent.

Insoluble or with difficulty soluble both in water and acids are the sulphates of baryta, strontia, lime, the oxide of lead and of a few rare oxides. These are decomposed by ignition with carbonate of soda, giving rise to sulphate of soda and a carbonate, which may be separated by water.

General determination of sulphuric acid. This is always effected by means of chloride of barium, the fluid having been previously rendered slightly acid by hydrochloric acid in order partly to decompose any carbonate that may be present and secondly to promote the deposition of the sulphate of baryta. Notwithstanding all this, it sometimes happens, even when the precipitate has settled properly, that a part of it passes through the filter, rendering the filtrate turbid, whilst another part fills up the pores of the paper to such an extent, although the filtrate passes clear, yet the filtration is exceedingly slow, and if this be relieved by washing, the fluid becomes again turbid.

In order to obviate this, the clear supernatant fluid is first poured upon the filter, the deposit is then stirred up with boiling water, this is allowed to settle, and the clear fluid is again poured upon the filter. This operation is repeated; finally the deposit itself is placed on the filter.

The sulphate of baryta is washed with hot water and dried in the air, it is then removed as much as possible from the filter into a platinum crucible, the filter itself being incinerated on the lid of the crucible and the ashes thrown into the crucible with the rest.

The contents are now ignited, taking care to place a small

strip of platinum across the edge in order to promote the incineration of any small fibres of paper, as also, if by means of the carbon there should be formed a trace of sulphide of barium, to reduce this again to the state of oxide.

1. SULPHATE of BARYTA containing STRONTIA.

(HEAVY SPAR.)

The substance is first reduced to an impalpable powder and then placed in a weighed platinum crucible, it is now mixed gradually with three times its weight of dried carbonate of soda, also reduced to a fine powder; the mixture is stirred up intimately with a glass rod at each addition. The crucible is now covered and heated over a lamp until the contents fuse. As soon as the crucible has cooled, it is placed in a dish of water and heated in order to loosen the contents and get them out of the crucible.

This being effected, the contents are filtered, and the residue, consisting of carbonate of baryta and strontia, is thoroughly washed. The filter and its contents are now transferred to a beaker glass, covered with dilute acetic acid and digested, until the carbonates are dissolved, taking care to cover the vessel with a concave watch glass, in order to avoid all loss by evaporation. The filter is now taken out and washed by means of a washing bottle, and then the fluid is filtered; in case there is any undissolved substance left on the filter, it is dried, ignited and weighed; the amount is deducted from that originally started with. If the solution is somewhat dilute, it must be concentrated by evaporation in an evaporating dish; it is then mixed with an excess of hydrofluosilicic acid and a quarter of its volume of alcohol, and set aside for twelve hours, during which time the silicofluoride of barium is gradually deposited. At this stage the fluid is filtered on a weighed filter, and dried at a temperature of 248°F ; the residue is washed for a short time in cold water containing a little alcohol, it is then dried in the air, and afterwards in the drying apparatus at a temperature ranging between 248°F .

and 266°F., until its weight no longer changes.

The filtrate in a dish (preferably of platinum) is mixed with a little sulphuric acid and evaporated to dryness; the residue, consisting of sulphate of strontia, is placed in a platinum crucible and ignited at a low temperature. Or after the addition of the sulphuric acid, a volume of tolerably strong alcohol equal to that of the fluid is mixed with it; the sulphate of strontia is then removed by filtration, washed with dilute alcohol, dried, ignited and weighed.

The sulphuric acid in the alkaline fluid, to which hydrofluoric acid has been added in excess, is determined in general by methods previously given.

2. SULPHATE of STRONTIA containing also BARYTA and LIME.

(CELESTINE.)

The substance is reduced to an impalpable powder, as in the preceding example, then fused with carbonate of soda; the fused residue is next washed in water in order to dissolve all that is soluble; the mixture is filtered and the sulphuric acid is determined in the alkaline filtrate.

The carbonates of the three earths remaining on the filter are transferred to a dish, and whatever adheres to the filter is washed with water containing a few drops of hydrochloric acid, and added to the rest. A sufficient quantity of dilute sulphuric acid is now added, and the whole is evaporated until all excess of acid has been volatilized. A solution of carbonate of ammonia or of bicarbonate of potassa is next added to the sulphates; and the mixture is set aside for at least twenty-four hours at a temperature below 68°F., taking care to stir it frequently. By this treatment the sulphate of baryta remains unchanged, whilst the sulphates of strontia and lime are converted respectively into carbonates. The mixture is filtered, washed with a very dilute solution of carbonate of potassa, then with pure cold water, until the wash-water by the addition of hydrochloric acid no longer indicates the pre-

sence of chloride of barium. The whole is then treated in the cold with dilute hydrochloric acid; and the sulphate of baryta is removed by filtration, washed, dried and ignited.

The solution of strontia and lime is evaporated to dryness on the water bath; the free acid is driven off; the two chlorides are then dissolved in the smallest quantity of water possible, to which is added a solution of about fifty times its volume of sulphide of ammonium; the mixture is then set aside in the cold for twenty-four hours, stirring it frequently; or it may be boiled for some time, taking care to replenish the water lost by evaporation. By this means the sulphate of strontia, which is insoluble in solutions of the alkaline sulphates, is completely separated, whilst the sulphate of lime remains dissolved. The former is separated by filtration and washed with a concentrated solution of sulphate of ammonia until the wash-water no longer becomes turbid with oxalate of ammonia. To the filtrate, diluted with water, ammonia and oxalic acid are added, taking care that the fluid still retains no alkaline reaction; the mixture is then set aside at a gentle heat, until the oxalate of lime has entirely settled. A few drops of oxalic acid are added in order to be certain that the whole of the lime has been precipitated; the latter is then separated by filtration, washed with hot water, dried and ignited, at first over the lamp with access of air, then for a few minutes over a gas-blast, by which it is converted into pure lime.*

Instead of treating the sulphate with a solution of carbonate of ammonia or of carbonate of potassa in the cold, it may be boiled with a solution of carbonate of potassa to which about one-third of sulphate of potassa is added. The solution is allowed to settle; the clear part is filtered, and the filtrate is boiled with a solution of the two salts. The mixture is washed from the sulphate of baryta and from the carbonates of strontia and lime; the subsequent process has been given.

If the amount of lime exceeds a few decigrammes, or if the gas-blast is not at hand, the oxalate of lime is converted by gentle ignition, &c., into carbonate of lime. (Vide page 119).

3. ALUM.

(SULPHURIC ACID, ALUMINA, POTASSA, AMMONIA, WATER.)

a. *Estimation of the sulphuric acid.* This is effected by the general method already prescribed.

b. *Estimation of the alumina and of the potassa.* A fresh quantity of the salt is dissolved in warm water in a beaker glass, to this is added a sufficient quantity of ammonia as to give the solution an alkaline reaction. The fluid is filtered into a dish; the residue (alumina) on the filter is repeatedly washed with boiling water, it is then dried and ignited. The filtrate is evaporated to dryness; the residue is placed in a platinum crucible, and the evaporating dish is rinsed out with the smallest possible quantity of water, which is placed in the crucible with the residue. The residue is again evaporated to dryness, taking care, however, not to cause the mixture to boil; as soon as the contents are dry, they are ignited over the lamp at a pretty high temperature.

Since the sulphate of potassa, which is thus obtained, has an acid reaction from the sulphuric acid derived from the alumina-salt, and since this excess of acid, or at all events a large portion of it, is but slowly driven off by ignition, the latter is performed in an atmosphere of carbonate of ammonia, which materially expedites the volatilization.

At the termination of the operation a strip of platinum is hung over the edge of the crucible; the lower end of the leg of this strip within the crucible is bent slightly upwards so as to form a sort of stirrup on which is placed a small piece of carbonate of ammonia; the crucible is now covered with its lid, quickly heated and raised to vivid ignition. After a few minutes the lid is taken off in order to see if there are still fumes of sulphuric acid given off, which are easily made visible by simply breathing into the crucible. If this should be the case, the operation is repeated with a second piece of carbonate of ammonia; finally the strip of platinum is withdrawn, and the crucible with its cover on is allowed to cool, whereupon it is immediately weighed. The amount of po-

tassa is computed from the amount of neutral sulphate of potassa found.

Instead of carbonate of ammonia, a saturated solution of sulphide of ammonium, recently prepared, is almost to be preferred as a precipitant of the alumina.

c. *Estimation of the ammonia.* A fresh quantity of the salt is dissolved in a flask in water and then boiled with a solution of either soda or potassa. The ammonia set free is caused to pass through a tube bent twice at right angles into a Woulfe's bottle and to dip into a solution of dilute hydrochloric acid filling the bottle about one-third full; the bottle itself is kept cool by being placed in a vessel of cold water; it is also connected with a second two-necked bottle by means of a tube reaching down but a few lines into the same dilute acid. The gas is caused to be evolved regularly but slowly by boiling the mixture for some time. As soon as it may be presumed, that all the ammonia has been expelled, the flask is disconnected from the tubes and the lamp removed. The fluids in the two bottles are poured into an evaporating dish, and evaporated in this nearly to dryness and then transferred to a platinum crucible and evaporated to dryness on the water bath. The residual chloride of ammonium is completely dried at a temperature of 212°F. and then weighed.

d. *Estimation of the water.* If the amount of water is not to be determined by the loss, the salt must be ignited. Since, however, the sulphates of the weaker bases, as for instance of alumina, also lose sulphuric acid by ignition, this operation alone would produce an erroneous result. The salt, therefore, is first mixed with oxide of lead, and then ignited; this retains the sulphuric acid. The pulverized salt is weighed and placed in a capacious porcelain crucible. In another crucible about six times the amount of powdered oxide of lead is placed, this is heated, but without fusion; it is then allowed to cool in the covered crucible, and afterwards it is accurately weighed. The powdered salt, in its crucible, is

now mixed with this oxide of lead by means of a glass rod, the last portions being poured upon the salt by shaking. Finally the crucible, which previously had contained the oxide of lead, together with any adhering particles, is weighed, in order to ascertain with accuracy the quantity added to the salt. The mixture is heated for some time at rather a high temperature, and as soon as it is cold, it is immediately weighed. Subtracting the weight of the contents from that of the salt and oxide of lead together will give the weight of the water.

4. MANSFELD BLACK VITRIOL.

The bases of this salt, which crystallizes in dark blue-violet crystals, having the same form as those of sulphate of iron, out of the mother liquor of roasted copper-ores from which sulphate of copper has already been extracted, are: oxide of copper, protoxide of iron, protoxide of manganese, oxide of cobalt, oxide of nickel, oxide of zinc and magnesia.

In order to undertake the analysis of this complicated compound, a weighed portion of the salt is dissolved, a little hydrochloric acid is added, and then the copper is precipitated by hydrosulphuric acid. The filtration and the further treatment of the sulphide of copper are given in detail, page 52. The filtrate from the sulphide of copper is received in a dish and concentrated by evaporation; the protoxide of iron is then oxidized by nitric acid, and the evaporation is continued until all excess of acid is expelled. The fluid is then very much diluted with water, and the sesquioxide of iron is separated from the remaining bases by means of carbonate and acetate of soda (vide page 67).

The fluid filtered from the basic salt of iron is treated with an excess of carbonate of soda, and heated to boiling. By this means all the bases present are thrown down; these are separated by filtration, washed with hot water, and dissolved in excess of acetic acid. A current of hydrosulphuric acid is now passed through the dilute solution, which precipitates the

zinc, as sulphide, from the rest of the metals (vide page 105). After the expulsion of the fumes of hydrosulphuric acid by heat, carbonate of soda is added, which precipitates the oxides of manganese, nickel and cobalt and also magnesia. The dried and ignited residue is mixed in a porcelain crucible with sulphur, and the mixture is ignited in hydrogen gas. The sulphide of manganese and the magnesia are now dissolved out by means of dilute hydrochloric acid, and finally nickel and cobalt, remaining undissolved as sulphides, are separated from one another by the method given on page 100, if their amount is large enough.

Acetate of soda is added to the solution containing manganese and magnesia; the mixture is heated, and a current of chlorine is passed through it. The dark-colored fluid is now supersaturated with ammonia and boiled in order to drive off most of the free ammonia. The separated oxide of manganese is converted by ignition into the sesquioxide of manganese (the double protoxide and binoxide); whilst the magnesia is precipitated from the filtrate by means of phosphate of soda.

OBSERVATION.—The filtrates from the precipitates produced by carbonate of soda are tested with ammonia, sulphide of ammonium and phosphate of soda, to ascertain whether all the metals and magnesia have been removed.

A separate quantity of the vitriol is required for the determination of the amount of sulphuric acid.

VI. PHOSPHATES.

The combinations of phosphoric acid with bases belong in general to a class of substances that is more difficult than the rest to analyze. For not only is the determination of the acid itself never quite accurate when precipitated by means of a base (lime, baryta, and oxide of lead), with which it forms an insoluble combination, owing to the solvent action exerted by other salts, particularly that of ammonia, on the precipitated phosphate, but it is also very difficult in many cases to separate the phosphoric acid from the base in combination

with it, and more especially so from the alumina and magnesia; and these difficulties increase if the substance contains other components, as for instance, fluorine or silicic acid.

Those metallic phosphates are the easiest to analyze, whose bases can be precipitated from an acid solution by means of hydrosulphuric acid, as for instance the phosphates of the oxide of copper, of silver and of lead, &c. They are dissolved in an acid; the metal is then precipitated by hydrosulphuric acid from the dilute solution; and the amount of phosphoric acid in the filtrate is determined from the sulphide. The phosphates of silver and lead may be examined by separating the bases by means of hydrochloric acid or sulphuric acid; the same operation, too, may be applied to the phosphates of baryta, strontia and lime.

1. PHOSPHATE of LIME with CHLORIDE and FLUORIDE of CALCIUM.

(APATITE.)

a. *Estimation of the lime and phosphoric acid.* The mineral is reduced to an impalpable powder and then dissolved by digesting it in hydrochloric acid. If there is a small quantity of insoluble residue (of quartz, &c.), the solution is diluted and then filtered; the residue on the filter is well washed, dried, ignited and weighed; the amount is deducted. The acid solution is mixed with a proper amount of sulphuric acid and with three or four times its volume of alcohol. By this expedient the whole of the lime is precipitated as sulphate. The mixture is set aside for twelve hours, and then filtered through paper moistened with alcohol; the residue is washed with alcohol. As soon as the residue is dry, it is ignited and weighed; from the weight the amount of lime is computed.

The quantity of hydrochloric acid must not be greater than what is required to effect the solution. The specific gravity of the alcohol used in this experiment to produce the total precipitation of the sulphate of lime is 0.80. The precipitate

having thoroughly settled, the clear liquid is tested with alcohol and a little sulphuric acid to ascertain whether all the lime has been removed.

The filtrate from the sulphate of lime is diluted with water, heated for some time in order to drive off the alcohol, and then supersaturated with ammonia. This ought to produce no precipitate; but should there be any (phosphate of lime), it must be removed by filtration, dissolved in a few drops of hydrochloric acid and decomposed by means of alcohol and sulphuric acid. To the alkaline fluid an appropriate quantity of a solution of sulphate of magnesia, chloride of ammonium and ammonia (magnesia mixture) is added; the vessel is then set aside for a few hours at a temperature of 86°F.; after which the double phosphate of ammonia and magnesia is separated from the fluid by filtration and then thoroughly washed with a mixture of one part of ammonia and three parts of water applied warm. As soon as this substance is dry, it is rubbed off from the filter into a platinum crucible; the filter itself is folded together and placed on the top, the crucible is loosely covered and gently heated for some time and then the temperature is gradually raised to ignition, the cover in the meanwhile being pushed back over half the entrance and a strip of platinum foil placed over the edge. (If the precipitate is heated too quickly, it will remain grey.) By ignition the salt is changed into pyrophosphate of magnesia, from which the phosphoric acid may be computed.

b. *Estimation of the chlorine.* The fine powder is digested with nitric acid, taking care to apply only a very gentle heat, in order not to expel any of the chlorine. The fluid is then diluted and filtered; and a solution of nitrate of silver is now added, as long as there is any precipitate. The vessel is finally set aside in a warm place in order that the precipitate may completely settle. The fluid is now filtered through a weighed filter and dried at a temperature of 248°F.; the chloride of silver is thoroughly washed, then dried, in the the first place in the air, afterwards in the drying apparatus

at a temperature of $248-266^{\circ}\text{F.}$, until it ceases to lose any weight. From this, its final weight, the amount of chlorine is computed.

The fluorine can not be determined by any direct method. Its amount is computed, by first computing, from the phosphoric acid found, the amount of $3\text{CaO} + \text{PO}_5$ and, from the amount of chlorine found, the quantity of CaCl ; the rest of the calcium is to be regarded as originally in combination with fluorine, forming fluoride of calcium.

2. BONE BLACK.

(LAMP BLACK.)

A mixture of phosphate and carbonate of lime, carbon and sometimes also phosphate of lime containing hygroscopic water, sand and other impurities. The small quantities of magnesia, soda, fluorine and sulphuric acid, occurring in the organic mass of bones, are not taken into consideration here.

a. A quantity of the powder is dried at a temperature of 248°F. , until its weight remains constant.

b. Another quantity is decomposed in a carbonic acid apparatus (vide Carbonates) by means of hydrochloric acid. The loss of weight of the apparatus determines the weight of the carbonic acid. The contents are diluted, placed on a weighed filter, and the residue is washed with hot water, it is then dried at a temperature of 248°F. , ignited in a current of air in order to burn off the carbon, and weighed. The substance thus obtained generally consists of sand. The difference gives the amount of carbon.

The solution in hydrochloric acid is next mixed with ammonia in order to neutralize the largest portion of the free acid, but it still must retain a slight acid reaction; acetate of soda is now added and then the whole amount of lime is precipitated by oxalate of ammonia. As soon as the precipitate has completely settled, it is removed by filtration, washed with hot water and dried. The dry residue is now placed in a platinum crucible, and the filter is incinerated on the

lid and the ashes are poured to the rest in the crucible. The mass is now covered up with the lid and heated very slowly, finally the lower part of the crucible is made red hot and retained at this temperature for some time. By this means the oxalate of lime is converted into carbonate of lime, which is weighed. Since it is possible, however, that by ignition it may have lost a small portion of carbonic acid, it is moistened with a few drops of a solution of carbonate of ammonia, dried and heated as before. If the weight now does not correspond with the first, the operation is repeated until the two last weights remain exactly equal. The amount of lime is computed from the quantity of carbonate found.

Ammonia is added in excess to the filtrate from the oxalate of lime. (If a precipitate is hereby formed, it consists of the double phosphate of ammonia and magnesia, which has to be removed by filtration and further treated as indicated on page 118. The amount of magnesia and phosphoric acid are computed from the quantity of the ignited salt.) The phosphoric acid is precipitated by the magnesia mixture as prescribed on page 118.

3. ACID PHOSPHATE OF LIME.

This name is given, though wrongly, to a technical preparation, which is used as a manure, and prepared by decomposing the substance of bones by means of acids. Its value is in proportion to the quantity of free phosphoric acid. It is a mixture of sulphate of lime, chloride of calcium and free phosphoric acid with water, containing almost always a small quantity of undecomposed phosphate of lime, also carbon, sand, &c.

Our task is simply to determine the amount of free phosphoric acid. An extract is made from about ten grammes by means of hot water, which is added until the filtrate has no longer an acid reaction. The filtrate is now diluted to a litre. One tenth part of this (100 c.c.) is now taken for the analysis. A sufficient quantity of chloride of calcium is add-

ed to the solution, and then an excess of ammonia. By this mode of proceeding all the phosphoric acid is precipitated as the phosphate of lime $3\text{CaO} + \text{PO}_5$, which is separated in a close vessel by filtration, thoroughly washed, dried, ignited and weighed. From this weight the amount of phosphoric acid is computed.

4. PHOSPHATE of the oxide of LEAD and CHLORIDE of LEAD together with ARSENIC acid and LIME.

(SEVERAL GREEN AND BROWN LEAD ORES.)

The analysis of such a compound is on the whole the same as that of apatite (1. example).

a. *Estimation of the oxide of lead, the lime, the arsenic acid and the phosphoric acid.*

The fine powder is dissolved in nitric acid; and a current of hydrosulphuric acid is then passed through the solution. As soon as the precipitate shows an admixture of yellow, it is submitted to filtration. It contains all the lead and a small quantity of arsenic. Hydrosulphuric acid is again passed through the filtrate; the precipitate now is sulphide of arsenic alone; the mixture is heated on a sand bath and then filtered. The operation of passing a current of hydrosulphuric acid through the filtrate, of heating and filtering is repeated until no longer any more sulphide of arsenic is thrown down.

The mixture of sulphide of lead and of sulphide of arsenic is placed in a small flask by the aid of the wash-bottle and digested whilst still moist with sulphide of ammonium, until all the insoluble substance is of a pure black color; the sulphide of lead is then separated from the solution by filtration, after which proceed as directed on page 104. The sulphide of lead is treated with sulphur in hydrogen as indicated, page 62; and the sulphide of arsenic is precipitated from the filtrate by means of hydrochloric acid and afterwards converted into the double arsenate of ammonia and magnesia (vide page 94.)

The filtrates from arsenic and lead contain still lime and phosphorus. In the first place the hydrosulphuric acid is expelled by evaporation, ammonia is then added to give the fluid a slight alkaline reaction, after which acetic acid is added in slight excess; the lime is now precipitated by oxalate of ammonia, and the phosphoric acid by magnesia salt (vide page 118).

b. *Estimation of the Chlorine.* The process is the same as in example 1.

5. PHOSPHATE of the protoxide of IRON, and WATER.

(BLUE IRON ORE.—VIVIANITE.)

The substance is reduced to an impalpable powder and placed in a platinum crucible, and then mixed with three or four times its weight of dry carbonate of soda, also reduced to a fine powder, the latter being added gradually, and then brought into intimate contact with the powdered ore by means of a glass rod. The mixture is ignited in the flame of a lamp, after which the melted mass when cold is digested with water, until all that is soluble is in a liquid state. The alkaline fluid, which contains phosphate of soda, is filtered from the residual (containing an alkali) oxide of iron; the latter is thoroughly washed, and then placed, together with the filter, in a beaker glass and digested with hydrochloric acid. The fluid is diluted with water, and filtered; it is now heated with chlorate of potassa in order to oxidize whatever portion of the protoxide of iron may be present. As soon as the fluid is cold, ammonia is added, which precipitates the sesquioxide of iron, which is separated by filtration, washed, dried and ignited.

The alkaline filtrate is rendered acid in a flask with hydrochloric acid, and then heated for some time in order to get rid of all the carbonic acid. Ammonia is now added in excess and the phosphoric acid is precipitated by the magnesia mixture (vide page 118).

Estimation of the Protoxide iron. By the method just

given the entire amount of oxide of iron is obtained in the form of sesquioxide. But since the original substance contains both the oxides of iron, one of them has to be separately determined. To accomplish this object the compound is dissolved in a close vessel by means of hydrochloric acid; and the solution is then submitted to the volumetric test with permanganate of potassa.

The amount of water is obtained from the loss.

OBSERVATION.—The phosphate of iron may also be analyzed by treating the solution with ammonia and sulphide of ammonium; the precipitated iron is then removed by filtration; and the phosphoric acid is determined in the filtrate. Nevertheless it is no easy matter to separate the sulphide of iron by filtration; it is easily oxidized, and the filtrate will naturally contain iron. On this account this method is less to be recommended here than with other metallic phosphates.

6. PHOSPHATE of the protoxide of IRON, protoxide of MANGANESE, LITHIA and SODA.

(TRIPHYLINE.)

The compound contains, moreover, small quantities of magnesia and potassa.

1. *Method.*—The substance in fine powder is dissolved by heat in concentrated hydrochloric acid. The solution is diluted, and whatever residue there may be (quartz, felspar, &c.) is removed by filtration; the filtrate is then boiled in a dish for some time with hydrate of baryta. Baryta is added until the fluid has a strong acid reaction, and a film of carbonate of baryta begins to form on the surface. The fluid is filtered hot, and the residue is washed for some time with hot water. The baryta precipitates the phosphoric acid, the protoxides of iron and manganese and the magnesia; in the solution there remain lithia and soda, together with the small quantity of potassa.

The precipitate together with the filter is digested with dilute hydrochloric acid, mixed with water and so much sulphuric acid as is necessary to precipitate any adhering baryta; after which the sulphate of baryta is separated by filtration. Ammonia is added in excess to the filtrate, and then a sufficient quantity of sulphide of ammonium, so that by heat-

ing well, the black precipitate thoroughly settles, and the supernatant fluid has a yellow color. The residue, consisting of sulphide of iron and sulphide of manganese, is filtered hot, taking care to hasten the operation as much as possible and to cover the funnel; it is then thoroughly washed with water containing a few drops of sulphide of ammonium, dissolved in hydrochloric acid, digested until all smell of hydrosulphuric acid has passed off, and finally the solution is submitted to filtration. The iron is then oxidized by means of chlorate of potassa; and the separation of iron and manganese is effected by means of carbonate and acetate of soda (vide page 67). The filtrate from the metallic sulphides is rendered slightly acid with hydrochloric acid, then heated in order to expel all the hydrosulphuric acid and filtered; finally the phosphoric acid is precipitated by means of ammonia and the magnesia mixture (vide page 118).

The alkaline filtrate from the precipitate of baryta is mixed with carbonate of ammonia and pure ammonia and warmed for some time in order to separate the baryta that had been dissolved; this is then removed by filtration and washed with hot water. Hydrochloric acid is added in excess to the filtrate, which is evaporated to dryness on the water-bath; the residue is placed in a platinum crucible and heated, but not to ignition, the crucible being well closed all the while. The chlorides of lithium, sodium and potassium, thus obtained, are then weighed. They are afterwards placed in a well stoppered vessel containing equal parts of concentrated alcohol and ether, and set aside for several days, taking care to shake the mixture frequently. By this means the chloride of lithium is dissolved. The mixture is then submitted to filtration on a weighed and covered filter; the chlorides of sodium and potassium on the filter are washed with alcohol and ether, then dried at a temperature of 248°F. and weighed. The difference in weight gives the amount of chloride of lithium.

If the small amount of potassa is also to be determined,

the separation is effected by chloride of platinum, as described hereafter (vide Silicates of alumina, lime, soda and potassa).

OBSERVATION.—This method has the same trouble as that mentioned in the preceding example, the somewhat difficult precipitation and separation of the sulphide of iron and the sulphide of manganese.

2. *Method.*—The substance reduced to an impalpable powder is dissolved in nitric acid; pure mercury is added to the solution, which is then evaporated to dryness on the water-bath. The evaporating dish is covered during the evaporation with a concave glass; and the amount of mercury taken must be sufficient to leave a little excess in the dry mass. If the latter still smells of nitric acid, it is moistened with water and again evaporated to dryness; and this operation must be repeated, until no more acid vapors are evolved, that is, until a glass rod moistened with ammonia no longer gives rise to white vapors when it is held over the dish. The residue is now covered with water, warmed, filtered and then washed until the wash-water, when evaporated to dryness on a piece of glass, no longer leaves any residue. The filter now contains all the phosphoric acid combined with protoxide of mercury, mixed with the nitrates of the protoxide and of the oxide of mercury and metallic mercury; in addition to these it contains a large portion of the oxide of iron; and in the filtrate are found the nitrates of all the bases previously in combination with the phosphoric acid.

The filter is dried together with its contents; the latter are then shaken into a capacious platinum crucible and mixed with about four times their weight of pulverized and dry carbonate of soda. The filter, containing still some adhering particles, is rolled together into a round ball and placed in the middle of the powder. Finally the whole is covered with a layer of carbonate of soda, and the crucible is covered up and heated in a place where the noxious vapors of mercury may escape, at first a long time at a gentle temperature, below ignition, taking care not to fuse the mass.* At last, however, the contents are ignited and thoroughly fused. As

*If the mass is not dry and is quickly heated, the crucible will be much corroded.

soon as the crucible is cold, it is placed in water and warmed. By this treatment all is dissolved with the exception of a quantity of sesquioxide of iron, which is removed by filtration and for the present set aside. Hydrochloric acid is now added to the filtrate to give it an acid reaction; and the phosphoric acid is precipitated by ammonia and the magnesia mixture. The filtrate from the bases, which contains also a certain amount of the nitrates of the protoxide and of the oxide of mercury, is evaporated to dryness; the residue is heated in order to volatilize the mercurial salts (observing the precautions above-mentioned for the escape of the mercurial vapors); hereupon it is mixed with crystallized oxalic acid and a little water, concentrated, gradually heated and finally ignited; that which is soluble is extracted with hot water.

The residue consists of the sesquioxide of iron, the oxide of manganese and magnesia; whilst the alkalies as carbonates will be found dissolved in the fluid. These, together with the oxide which had been previously set aside, are dissolved in hydrochloric acid; the diluted solution is then mixed with acetate of soda and heated, whilst a current of chlorine is passed through it to saturation. Ammonia is now added in excess; and the mixture is then boiled to expel all the free ammonia. The oxides of iron and manganese are removed by filtration; dissolved in hydrochloric acid to which a little alcohol has been added, then separated by carbonate and acetate of soda (vide page 67). Magnesia is precipitated from the filtrate by means of phosphate of soda (vide page 137).

The solution of the carbonates of the alkalies are decomposed by hydrochloric acid and evaporated to dryness; and as soon as the weight of the chlorides has been determined, they are separated by the method already given.

7. PHOSPHORIC acid, ALUMINA, OXIDE of IRON, MAGNESIA.

There is no salt in which phosphoric acid so easily escapes detection as in the phosphate of alumina, from the fact that

It comports itself in regard to several reagents like pure alumina. Especially does its analysis present difficulties, which increase in proportion according as the oxide of iron, lime and magnesia are also present. These constituents occur not only in a few rare minerals (Kalaït, Wavellite, Lazulite, Chiledrenite, &c.), but also in soils; and several bog iron ores contain, besides the constituents mentioned on page 65, alumina.

The substance is mixed in a platinum crucible with an equal quantity of pure silicic acid and six times its weight of carbonate of soda, it is then gradually heated, and finally ignited.* As soon as the mass is cold, it is digested with water, in order to dissolve out all that is soluble, and then filtered. The filtrate is heated with an addition of chloride of ammonium, whereby silicic acid and alumina still remaining are precipitated; the precipitate is also removed by filtration. The filtrate is first neutralized with hydrochloric acid, and then with ammonia; after which the phosphoric acid is precipitated by the magnesia-mixture. The residue on the two filters, consisting of silicic acid, alumina, oxide of iron, lime and magnesia, are brought together and dried; the dried mass is placed in a dish (also the ashes of the two filters), digested in hydrochloric acid, and evaporated on the water-bath to dryness. The dry mass, when cold, is moistened with acid and, after standing for some time, it is heated with water and filtered.

As soon as the silicic acid has been removed, chloride of ammonium is added to the filtrate in proportion to the magnesia present; the fluid is then neutralized with ammonia in excess and boiled until all fumes of ammonia disappear. After filtration, the oxide of iron and alumina remain on the filter, these are washed with hot water, dried, ignited and weighed. The simplest method of determining the relative proportion of each of these two substances consists in redu-

*If the materials are found in solution of hydrochloric acid, carbonate of soda is added to neutralize the solution; this is then evaporated to dryness. The residue is placed in the crucible and mixed with the silicic acid and four times its weight of carbonate of soda.

cing a weighed quantity to an impalpable powder and then to heat it with hydrochloric acid and zinc, and finally to estimate the amount of the chloride of iron volumetrically. The difference of weight is that of the alumina.

Ammonia and oxalic acid precipitate the lime from the filtrate (vide page 131), whilst magnesia is thrown down with phosphate of soda (vide page 133).

VII. CARBONATES.

Estimation of the carbonic acid.—The amount of carbonic acid is frequently computed from the loss incurred when the bases in combination with it are determined directly, in case the substance contains no water, or when the degree of oxidation of the compound is already known.

If, however, the estimation is to be made by a direct method, this can be effected essentially in two ways:

- 1.) by igniting the substance, whereby the carbonic acid is expelled, and its weight determined by the amount of loss;
- 2.) by means of an acid, which in like manner drives off the carbonic acid; the amount of the latter, too, is found in a similar manner.

1. *Estimation of the carbonic acid by ignition.*

This method is far from being applicable to all carbonates. It presupposes that carbonic acid may be expelled by a moderate red heat, which is not the case, for instance, with the salts of the alkalies, of baryta, strontia and with difficulty with carbonate of lime; and furthermore that the remaining base undergoes no change, is not raised to a higher degree of oxidation, a circumstance that does not take place with the salts of the protoxides of iron and manganese and of the oxide of cobalt. If nothing of this sort does occur, the ignition is effected in a small crucible over the lamp, taking care to repeat the operation, after the weight has been determined, in order to be certain that the ignition the first time had not

been stopped too soon, which is known by the fact that the weights in both cases remain the same.

The direct determination of carbonic acid, in general, is seldom undertaken, and especially is this the case with those carbonates, whose bases suffer some change when ignited in the air. When such a determination has to be made, the ignition must be performed in some other indifferent gas, for instance, in carbonic acid itself and not in air.

If the carbonate, whose acid is to be determined by ignition, contains also water, it is ignited in a small glass retort or some other similar apparatus, attached to a receiver containing chloride of calcium.

2. *Estimation of the carbonic acid by another acid.*

Since the stronger acids liberate carbonic acid from all its combinations in the form of gas, they are had recourse to in all those cases in which the ignition of the substance is not applicable. This method is two-fold: either the *volume* of the evolved gaseous acid is determined over mercury in a graduated tube; or the *loss of weight of the apparatus*, which is caused by the evolution of the gas, is ascertained. The first method is not so frequently used, because it presupposes that the mercurial apparatus is always at hand, and especially a practical experience in analytical investigations with gases.

The second method is the one in general use. Although in principle it is exceedingly simple, yet certain precautions must be taken, especially such as aim to prevent the escape, along with the carbonic acid, either of water or of a part of the acid employed in producing the decomposition in the form of vapor. On this account the whole arrangement must be of such a nature as to be easily placed on a sensitive balance and weighed.

Among the various forms of apparatus for this purpose we give preference to that of Geissler. It consists of three parts: the flask, the vessel for the acid, and the drying apparatus. The first is a small flask with a flat bottom, in which the substance is weighed and decomposed by the acid. It has two

necks; through one of these a glass tube passes and extends nearly to the bottom of the flask, terminating here with a small orifice; but on the outside of the flask this tube is widened out into a cylindrical shape for the reception of the acid employed to produce the decomposition. In order that the acid may be made to flow or drop at will into the flask, a long narrow glass tube, open at both ends, leads through it, the raising and sinking of which regulates the flow of the acid. The drying apparatus, consisting of two small cylinders, is fitted into the second neck; it is partly filled with concentrated sulphuric acid and so arranged, that the carbonic acid, as it is evolved, has to pass through it and is thereby dried. The separate parts of this apparatus are fitted into each other air-tight by grinding.

When about to be used, the flask is weighed alone, then the substance in rough powder is poured into the flask, which is again weighed; the difference is the weight of the substance. A small quantity of water is now poured upon the powder; acid (in general hydrochloric acid) is next introduced into the vessel intended for its reception; this acid, although concentrated, must not emit any fumes;* the acid vessel is placed on the flask; the drying apparatus is adjusted in its place; and finally the whole arrangement is accurately weighed. By letting air into the glass tube† a small quantity of acid is allowed to flow into the flask gradually so as not to give rise to a too rapid current of gas, and this is continued until there is no longer any effervescence, and the carbonate is dissolved, with the exception perhaps of a small insoluble residue of some foreign material. The apparatus is now filled with carbonic acid; and the fluid in the flask is saturated with the gas. The flask therefore is heated but never to boiling in order to expel all the carbonic acid from the apparatus; this is effected by taking the cork out of the tube and

*The same apparatus is used for the analysis of black oxide of manganese described, page 70; but in this case sulphuric acid is used to produce the decomposition.

†Even when the terminal point of the acid receiver dips into the fluid, it is necessary to close the tube previously with a cork, &c.

drawing through a current of air at the extremity of the drying apparatus either with the mouth or by means of the aspirator; a tube filled with lumps of potassa is attached also to the glass tube. The loss of weight which the apparatus has suffered is owing to the carbonic acid that has been expelled from the carbonate.

The fluid in the flask may in general be employed for the determination of the bases.

1. LIME, MAGNESIA, CARBONIC ACID.

(BITTERSAP, DOLOMITE.)

A weighed quantity of the substance in powder is placed in a flask and dissolved in hydrochloric acid, applying a gentle heat until all the carbonic acid has been driven off, and, in case there should be any insoluble residue, on the addition of a few drops of acid there should be no more gas eliminated. The fluid is then diluted; the insoluble residue is removed by filtration; it consists chiefly of quartz, which is to be well washed.

Ammonia is added to the filtrate until an alkaline reaction is produced on litmas paper, or until there is a decided smell of this alkali; then a solution of oxalic acid is added gradually in order to precipitate the lime, and until no longer any precipitate is produced by this reagent. But even at the end of the operation the fluid must be alkaline, otherwise a part of the lime would remain in solution, on which account it may be necessary towards the conclusion to add more ammonia. The vessel is set aside for a number of hours in order that the precipitate may settle completely and the fluid become quite clear; the latter is then tested with a few drops of the precipitant to ascertain whether it contains any more lime.

The fluid is poured upon a filter and afterwards the oxalate of lime; the vessel that had been used is then thoroughly rinsed out by means of a feather and the wash-bottle; and the residue on the filter is washed with hot water until a few

drops of the wash-water, when evaporated to dryness on a piece of platinum foil, leave no observable marks. The residue is finally dried in the air and afterwards at a low red heat in order to convert it into carbonate of lime.

But since the residue, if submitted to a more intense red heat, is apt to lose a part of the carbonic acid, and the weighing of such a mixture of carbonate of lime and caustic lime would in every case give an incorrect result, it is necessary to employ several precautions whilst heating the precipitate.

As soon as the dried oxalate of lime has been shaken off from the filter as much as possible into a platinum crucible, the filter itself is burned on the lid of the crucible, and the ashes are added to the rest in the crucible, which is now thoroughly covered, and gradually heated over the lamp until the lower part of the crucible is raised to a low red heat, at which temperature it is kept for some time. After it is cool, it is weighed. The contents are then moistened with a few drops of a solution of carbonate of ammonia and then they are heated again as before. If the two weights exactly correspond, it is evident that no carbonic acid has been lost in the first experiment; but should not this be the case the correction and heating are repeated until the two weights are exactly the same. From the carbonate of lime thus received, the weight of the lime in the substance is computed.

The conversion of the oxalate of lime into caustic lime is much more quickly effected by the use of a powerful gas-blast. As soon as the precipitate has been already strongly ignited in the air, the covered crucible is held in the gas-blast from a few minutes to a quarter of an hour according to the quantity of lime. The crucible is weighed, and the ignition repeated. The lime at this stage, when first moistened with water, must dissolve in acids without effervescence. If the amount of lime is pretty large, it is advisable to moisten the contents of the crucible with water after ignition for the first time and then to apply a gentle heat, before it is a second time ignited.

There remains now only the magnesia to be determined in the filtrate from the oxalate of lime. A rather large quantity of phosphate of soda is added to the fluid, and dissolved by the application of heat; then ammonia is added to the fluid which is now set aside for twenty-four hours. By this means the double phosphate of ammonia and magnesia is gradually thrown down. The residue is then removed by filtration and washed with a cold mixture of one part of ammonia (spec. grav. 0.96) and three parts of water, (because it is soluble to a slight extent in pure water alone) until the last drops, when evaporated to dryness on a strip of platinum, leave no marks behind. The contents of the filter are now dried on the filter, and afterwards ignited; the filter itself is incinerated, an operation which, owing to the saturation of the fibres of the paper with the salt is rather slow; the ashes are added to the contents of the crucible. At the beginning the crucible is covered, but afterwards the cover is removed, and a strip of platinum foil is placed over the edges in order to institute a draft of air. By this ignition of the precipitate ammonia and water are expelled, and a rapid extinction of flame is produced; finally there remains pyrophosphate of magnesia ($2\text{MgO} + \text{PO}_5$), from which the amount of magnesia is computed.

The filtrate is again mixed with phosphate of soda, is again set aside, and as a general thing is never thrown away, until in this way a certainty is obtained that all the magnesia has been precipitated. If there should be still any precipitate, it is placed with that, previously obtained, on the filter.

It often happens, that a carbonate of lime and magnesia contains also iron, either in mixture as oxide, or as a carbonate of the protoxide in isomorphous mixture. If the amount of iron is very small, it is either neglected, or it is found in the lime, which is dissolved in an acid and supersaturated with ammonia. The precipitation and filtration of the sesquioxide of iron must take place in a closed vessel (vide the following example). When the quantity of iron is large, the

process is the same as that in example second.

If when ammonia is added, at the beginning of the analysis, in excess to the solution there should be produced a light colored precipitate, it is magnesia, and it is caused by a deficiency of ammoniacal salt. The whole is then supersaturated with hydrochloric acid and again neutralized with ammonia.

2. PROTOXIDE of IRON, protoxide of MANGANESE, CARBONIC acid, LIME and MAGNESIA.

(SPATHIC IRON ORE, BITTERSPAR.)

The substance in powder is digested in a flask with hydrochloric acid, until by the addition of a few drops of acid no more change is observable, or until all is dissolved. The protoxide of iron (protochloride) is converted into the sesquioxide (chloride) by adding to the fluid, still hot, a small quantity of chlorate of potassa, until it assumes a yellow color and begins to smell of chlorine. The solution is now heated, and, in case there should be any insoluble substance (quartz, &c.), the latter is thoroughly washed, dried, ignited and weighed.

The solution is made very dilute in a capacious dish, and, being covered with a plate of glass, it is gently heated and so long mixed with powdered carbonate of soda, which is added in small portions at a time, until the color becomes a dark-red, and a part of the sesquioxide is precipitated as a basic salt. (The greater the quantity of iron compared with that of the manganese, the greater will be the amount of precipitate of the former, but the fluid must still always have a red color. When the amount of iron is small, in order not to go beyond the right point, carbonate of ammonia, at the last preferably in solution, must be added only as long as the fluid becomes colored.) Then a quantity of acetate of soda (from 2 to 10 grammes), corresponding to the proportion of iron, is added and the solution is heated to boiling. By this means all the sesquioxide of iron is precipitated as a basic salt,

whilst protoxide of manganese, lime and magnesia remain in solution. The latter is filtered whilst hot, and the residue is washed with hot water; but whatever adheres firmly to the dish is left there, and in this dish the filter, containing the washed residue, is placed and digested with dilute hydrochloric acid. This solution is filtered, and to the filtrate ammonia is added, this throws down the sesquioxide of iron which is washed with hot water, dried, ignited and weighed.

The filtrate, which contains the remaining bases, is again mixed with acetate of soda, gently heated and saturated with chlorine. Ammonia is added in excess, and the mixture is then boiled until the excess has all been expelled. The oxide of manganese is then removed by filtration, washed with hot water, dried and ignited at an intense red heat, by which it is converted into the protoxide. The filtrate is neutralized with ammonia, the lime is then precipitated with oxalic acid, and the magnesia with phosphate of soda (vide example 1.).

3. OXIDE of LEAD, CARBONIC ACID, WATER.

(WHITE LEAD.)

The purest white lead contains only traces of the acetate, sulphate and chloride of lead. But the common sorts contain heavy spar (which by solution in acetic acid remains undissolved), chalk, &c.

A part is ignited in a porcelain crucible. By this means a portion of the oxide of lead is obtained. Another part is used for the determination of the carbonic acid, for which purpose nitric acid is used as the solvent.

The amount of water is obtained by the loss of weight.

VII. BORATES.

In the analysis of borates either the base is alone determined, the acid computed out of the loss, or it is also determined in a direct manner.

In the first case the method to be selected depends on the nature of the base: if this is a metallic oxide proper, it is separated by hydrosulphuric acid; if it is the oxide of lead, baryta, strontia or lime, the separation is effected by sulphuric acid (and alcohol); and if it is magnesia and the compound is easily dissolved in an acid, the base is precipitated by phosphate of ammonia. In like manner almost all the borates both of the alkaline earths and of the metals may be decomposed by ignition with carbonate of soda; when treated with water the borate of soda is dissolved, and the base remains behind either free or in the form of carbonate.

But if the borate is a salt of an alkali, or if the compound is with difficulty dissolved in acids, it is converted by means of concentrated hydrofluoric acid into a mixed fluoride and borofluoride, which is heated with sulphuric acid, and then the base is determined either as a sulphate, or may be separated from this in an especial manner. I have used this method with great advantage in the analysis of the native borate of magnesia, that is, boracite.

•The direct determination of boracic acid by precipitation with a salt of one of the alkaline earths or of a metal, as may be done with so many other acids, does not succeed on account of the solubility and easy decomposition of such borate precipitates. It is only possible in the form of borofluoride of potassium, a method which was first proposed by Berzelius and afterwards improved by A. Stromeyer.

To the solution of boracic acid, which must not contain any other bases except the alkalies, half as much again of hydrated potassa as the amount of boracic acid, is added; after this pure hydrofluoric acid is added to the mixture in a platinum dish in excess, so that the fluid has not only an acid reaction, but exhales when heated acid vapors. The mixture is evaporated to dryness on the water-bath. A solution of one part of acetate of potassa in five parts of water is poured upon the residue, which is set aside for a number of hours at the common atmospheric temperature, stirring it frequently;

the borofluoride of potassium, that is thus thrown down, is separated by filtration on a weighed filter and washed with a similar solution, until the wash-water is no longer precipitated by chloride of calcium, and finally with concentrated alcohol. The salt is dried at a temperature of 212°F. , and from this the amount of boracic acid is computed.

If the solution of the boracic acid contains many salts, especially salts of soda or sulphate of potassa, it is well to heat the dried mass with the solution of acetate of potassa and to set it then aside from twelve to twenty-four hours, before it is filtered.

1. LIME, SODA, BORACIC ACID and WATER.

(BORONATROCALCITE, TIZA.)

The mineral contains, in addition, small quantities of potassa, chlorine and sulphuric acid.

a.—It is heated in a platinum-vessel with a mixture of hydrofluoric acid (or fluoride of ammonium) and sulphuric acid; it is then evaporated to dryness; and the residue is heated to long ignition. When treated with water a large portion of sulphate of lime remains undissolved; this is removed by filtration, afterwards thoroughly washed, dried, ignited and weighed. The remaining part of the lime in the filtrate is thrown down by means of ammonia and oxalic acid (vide page 131); the fluid is evaporated to dryness; the sulphate of soda is placed in a platinum crucible, ignited, and rendered neutral by means of carbonate of ammonia (vide page 113). If it be required to determine the small amount of potassa, which it contains, it is weighed and then converted into chlorides; the two alkalis are separated by chloride of platinum (vide Silicates, analysis by means of hydrofluoric acid).

b.—The amount of water is determined by igniting a part of the substance either alone or with a weighed quantity of oxide of lead.

c.—For the determination of the chloride and the sulphuric acid separate portions of the substance are respectively

employed; the former is determined by means of nitrate of the oxide of silver, the substance having been previously dissolved in cold dilute nitric acid (vide page 118); the latter by chloride of barium in a dilute solution of hydrochloric acid.

The amount of boracic acid is derived from the loss. If it is to be determined directly, the substance is dissolved in hydrochloric acid; the lime is precipitated with carbonate of potassa; and the filtrate is treated as directed, page 136.

2. MAGNESIA, BORACIC acid, CHLORINE, WATER.

(STASSFURTHITE.)

a.—The substance previously reduced to a fine powder is fused with four times its amount of pure carbonate of potassa, the mass is then digested in hot water and filtered; magnesia remains behind and is washed in hot water, dried, ignited and weighed. The boracic acid in the filtrate may be determined directly according to instructions given on page 136.

b.—Another portion is dissolved in dilute nitric acid from the solution of which the chlorine is determined as in the preceding example.

c.—If the water is to be determined directly, it is effected by ignition with oxide of lead (vide page 114).

IX. SILICATES.

The compounds of silicic acid, comprehending as they do a large portion of the minerals as well as all the slags and vitreous products of fusion, are in analytical chemistry of particular importance, and so much the more so from the fact, that the separation of the silicic acid from the bases in combination with it requires different methods in the different cases, and in general is frequently no easy matter. For although alone, when ignited, it may be regarded as insoluble

in water and in almost all acids, yet it occurs, when its salts have been decomposed, in a condition in which this property of insolubility is no longer so distinct a characteristic, so that a certain smaller amount remains behind in acid solutions, and is separated at the same time with the precipitated bases, thus rendering the separation and accurate determination of this substance a difficult operation.

All silicates, by reason of their comportment with acids (hydriodic, nitric, sulphuric) are divided into two classes:

A. Those which are decomposed by them, and

B. Those which are not decomposed by them.

When a silicate is decomposed by an acid, the silicic acid is separated, whilst the bases, previously in combination with it, are dissolved in the stronger acid. But the silicic acid thus precipitated has not always the same appearance; sometimes it is thrown down in a *gelatinous form*, so that after digestion in the proper amount of acid, the silicic acid forms on cooling a stiff sort of jelly. Silicates of this description are said to *gelatinize*. In other cases the silicic acid, when it is precipitated, assumes a *slimy, flocculent or pulverulent appearance*.

The silicates, that thus undergo decomposition in acids, form the smaller class of the two; belonging to this class may be reckoned many minerals, especially those containing water, and designated as the family of the Zeolites (Mesotype, Apophyllite, Analcime, Chabasite, Stilbite, Heulandite, &c.), and besides these many others. In this class also may be comprehended many of the artificially formed silicates, especially several slags, such as iron slags and artificial ultramarine, &c.

With the majority of these substances, yet not with all, especially with the hydrous class, the decomposition by means of acids is either entirely prevented by *ignition* or considerably impaired, and it thus frequently happens, that the analysis can not be continued with the same portion which had been ignited for the estimation of the water. That this

is not the case with those which owe their formation to a fusing process, is self-evident.

On the other hand it happens, that a silicate of the second class, which is not decomposed in acids or only with difficulty decomposed, *may be decomposed by acids after ignition or fusion* and as a rule so completely as to gelatinize. This interesting fact was observed by Fuchs, von Kobell and Magnus in regard to Epidote, Garnet and Vesuvian; and I have also confirmed the fact in reference to Axinite. This change is allied to the transition of the silicate from the crystalline to the amorphous condition, and is accompanied with a diminution of its specific gravity. On this account ignition or fusion may be with propriety used in the analysis of such minerals; for the process of those, which undergo decomposition by means of acids, is more simple than of those in the opposite condition.

Nevertheless it must be acknowledged, that the line of demarcation of these two classes of silicates in reference to their comportment with acid, is not absolutely fixed, for, strictly speaking, there is not a single one in the pulverized condition that can resist the continued action of a concentrated acid, especially when heated; and the felspar and micacious minerals, hornblende and augite, which belong to the second class, suffer in this case, according to the duration of the action, a more feeble or intense decomposition. If, therefore, our classification is to be regarded as correct to a certain extent in accordance with science, we must in every case comprehend in the category of silicates which suffer decomposition by means of acids only those, whose decomposition proceeds *easily and quickly*, although this takes place in very different degrees among the different substances placed in this class, so much so indeed that sometimes a silicate, which may be accurately enough decomposed by means of an acid for a qualitative investigation, must not be treated by the same means for a quantitative analysis, but has to be first fused with an alkali.

It must not, however, be supposed when a silicate is decomposed by an acid, that *all* the silicic acid is set at liberty, nor that that, which is precipitated, is always *pure* silicic acid. As regards the first point it is to be observed, that there remains in the acid fluid no inconsiderable part of silicic acid in solution, which is subsequently thrown down together with the bases present. On this account it becomes necessary, after these precipitated bases have been ignited and weighed, to separate the small amount of silicic acid mixed up with them; this is effected by digesting them respectively with an acid (hydrochloric acid), which leaves the silicic acid undissolved. But again here are the following troubles: on one side a portion of the latter is again dissolved; and on the other some of the ignited bases (alumina, sesquioxide of iron) are with difficulty soluble in acids, a circumstance which renders the separation any thing but easy and certain. Or the decomposed silicate is evaporated to dryness, so that the residue appears dusty; it is then treated with water, which dissolves the bases in combination with the acid used to produce the decomposition, but leaves the silicic acid undissolved. But in this case also a part of the latter is dissolved in the acid, although the quantity is small, and which in many cases may be neglected. But there is another difficulty when a decomposed silicate is evaporated to dryness, it is this, the weaker bases (alumina, sesquioxide of iron) are easily converted into basic salts or partly thrown down in the basic form, and in this condition are insoluble in water, consequently they remain in mixture with the silicic acid. It is therefore indispensable to moisten the dry mass, left by evaporation, uniformly with hydrochloric acid before it is treated with water, and to allow it to stand for an hour or so, in order that those bases may again combine with the acid which they had parted with. With silicates rich in iron it will, however, be easily observed, that, if the evaporation had been carried so far as to produce the red color of the sesquioxide of iron in the mass, even although treated with the acid, the

silicic acid can no longer be obtained free from oxide of iron. On this account it becomes necessary always to pay great attention to the temperature employed in the evaporation, and in cases like that just alluded to, it is safest to complete the work on a water-bath, only not forgetting, as already observed, to continue the heat so far as to produce a residue perfectly dry and of a dusty appearance.

As regards the second point, namely, that the precipitate produced by treating a silicate with an acid must not be, at once, looked upon as pure silicic acid, this point is of great importance in analysis, and it is only lately that it has been accurately recognized. Even when a mineral apparently has been so perfectly decomposed by an acid, that the silicic acid separates in the gelatinous form, it can not always be assumed with certainty, that this is pure silicic acid. But because this has been the rule hitherto, it is quite possible that the determination of the silicic acid in many minerals is not right. In order to be convinced that the silicic acid, obtained by decomposing a silicate by means of an acid, was pure, the acid so obtained was ignited and weighed, then boiled with a concentrated solution of carbonate of soda; this dissolved the silicic acid; the residue was regarded as undecomposed silicate and was deducted from the amount of silicic acid as well as from the amount of substance originally employed.

This may certainly be right, if the silicate employed for the analysis had not been previously reduced to a sufficiently fine powder. But even when the pulverization has been performed with care, and the mass has been decomposed with hydrochloric acid so well that it is not possible to find any undecomposed, hard and therefore gritty particles by means of a glass rod, it often happens, that silicic acid when boiled with carbonate of soda will leave an undissolved residue. It is thus that H. Rose* discovered, that silicic acid, obtained by the decomposition of titanite by means of hydrochloric acid, and treated with a solution of carbonate of soda,

leaves as much as thirty per cent of residue. The amount of this residue is at one time larger and at another smaller, although powder of the same degree of fineness is employed. If the silicate is easily decomposed by means of hydrochloric acid, and the silicic acid separates in a gelatinous form, the latter contains more of insoluble residue if the powder of the silicate is treated with highly concentrated hydrochloric acid, and the two are not intimately mixed together by continual stirring so that the gelatinous substance is soon formed. On the contrary the residue left, after boiling the silicic acid in a solution of carbonate of soda, is small if the powdered silicate has been stirred about for some time in a more dilute acid whereby the formation of the gelatinous substance is prevented from taking place, and especially if the acid is left to act on the powder as long as possible.

The combination of the residue in question is by no means that of the silicate; and, on this account, its weight in this state must not be deducted. It is only when the substance has not been previously reduced to a sufficiently fine powder, that a part may remain undecomposed and mixed with the silicic acid. Otherwise, however, this undissolved residue in the solution of carbonate of soda consists in general of silicic acid and small particles of the bases, and the amount of the former in the zeolites, according to H. Rose, is from 90 to 97 per cent; the remaining part is in general alumina and lime.

Of all the silicates those, which contain either titanitic acid or zirconic acid, appear to produce the largest quantity of such residues. As already mentioned, H. Rose has called particular attention to this circumstance in the analysis of titanite, and I have confirmed this result in the analysis of eudialite a silicate, containing zirconic acid, sesquioxide of iron, lime and soda in which the residue separated from the precipitated silicic acid appears to be at the same time a distinct compound,* as also of that of cerite, the half of whose silicic

*POGGEND. ANN. Vol. 63, page 142.

acid set free by hydrochloric acid consists of bases.*

If in the analysis of a silicate the amount of such insoluble residue is only very inconsiderable, the error indeed is not very great if it be regarded as undecomposed substance, and still smaller if it be regarded as silicic acid. But the error becomes more considerable in the examination of rocky materials consisting of a silicate, that may be decomposed by means of acids, and of another that resists their action. If the whole substance is treated with an acid, the insoluble portion consists of the silicate that can not be so decomposed and of the silicic acid of that portion that can be so decomposed. If the insoluble residue is now boiled in carbonate of soda, in order to dissolve out the silicic acid, a part of the latter remains in combination with small quantities of the bases, and this consequently will be the cause, in the analysis of the residue, of finding more silicic acid than properly belongs to the silicate not decomposable by acids.

There is a very simple and easy means of ascertaining the purity of the silicic acid obtained in analyses, which also may be employed with advantage in the subsequent investigation of the residues in question. It consists in the employment of hydrofluoric acid. If the silicic acid is covered with this acid in a platinum dish, and the fluid evaporated on a water-bath to dryness, there ought to be no residue, if the silicic acid were pure, because it volatilizes as fluosilic acid. If, on the contrary, there is any residue, it consists of the silico-fluorides of the metals of the bases combined with the silicic acid. Finally sulphuric acid is added, which converts the silico-fluorides by heat into sulphates, which admit of being easily analyzed. Fluoride of ammonium may, with equal success, be substituted for hydrofluoric acid, which is mixed in a platinum crucible with the silicic acid and a little water and then heated.

We will now proceed to the special analytical processes for the two classes of silicates.

The bases contained in these substances are in general the following :

Potassa,
Soda,
Lime,
Magnesia,
Alumina,
Protoxide and Sesquioxide of Iron,
Protoxide and Binoxide of Manganese.

These bases rarely occur all together in one and the same silicate, but they are so common, and the mode of their separation so simple, that a qualitative analysis is seldom undertaken beforehand, and it is only necessary when there happens to be any doubt whether iron exists in the silicate in the form of protoxide or sesquioxide, or in both conditions at the same time, as also when it is of importance to ascertain the presence of such bases as occur only in certain silicates and for the separation of which the analytical process has to be modified. Of this nature are the following :

BARYTA (Harmotome, Brewsterhite.)*
STRONTIA (Brewsterhite.)
BERYLLIA (Helvine, Gadolinite, Orthite? Tschewkinite.)
YTTRIA (Gadolinite, Orthite, Tschewkinite.)
THORINA (Thorite.)
PROTOXIDE of CERIUM, OXIDE of LANTHANUM, OXIDE of DIDIMIUM (Cerite, Orthite, Gadolinite, Tschewkinite, Mosandrite.)
ZIRCONIA (Eudialite, Woehlerite.)
OXIDE of ZINC (Calamine, Silicious oxide of Zinc.)
OXIDE of LEAD (Thorite, Calamine, Lead Slags.)
OXIDE of BISMUTH (Eulytine, Silicate of Bismuth.)
OXIDE of COPPER (Diaptase, Chrysocolla, Allophane, Copper Slags, &c.)
OXIDE of URANIUM (Thorite, &c.)

Of Electronegative Bodies the following sometimes occur :

*In this list are only those silicates that can be decomposed by means of acids,

TITANNIC ACID (Titanite, Tschewkinite.)

TANTALIC ACID and NIOBIC ACID (Whoelerite.)

BORACIC ACID (Datolite, Botryolite, Rhodocite.)

PHOSPHORIC ACID (Ledererite? Eulytine?)

SULPHURIC ACID (Hauyne, Noseane, Lapis Lazuli, Sko-
lopsite, Ittnerite, Ultramarine.)

CARBONIC ACID (Cancrinite, Stroganowite.)

FLUORINE (Chondrodite, Apophyllite, Scapolite.)

CHLORINE (Sodalite, Eudialite, Pyrosmalite, Hauyne, La-
pis Lazuli.)

SULPHUR (Helvine, Hauyne, Noseane, Lapis Lazuli, Itt-
nerite, artificial Ultramarine and Slags.)

Water is sometimes a constituent of the silicates of this
class, and sometimes it is not.

When fluorine exists as a constituent of the silicate, certain
precautions have to be observed in the determination of the
silicic acid and the water; the same may be said also when
titanic acid and other rare oxides are in combination with si-
licic acid. The determination of the water, too, is modified
when chlorine, sulphur, sulphuric acid and carbonic acid are
present at the same time.

GENERAL RULES for the ANALYSIS of SILICATES.

Pulverization.—Every silicate, previous to the commence-
ment of its analysis, must be carefully reduced to an impalpa-
ble powder, so that neither under the pestle of the mortar
nor between the fingers it is possible to distinguish any grit-
tiness. It is only when this degree of fineness has been at-
tained, that a complete decomposition is to be expected, and
it is necessary that the decomposition must be complete, be-
cause the amount of that which is not decomposed and which
remains in mixture with the precipitated silicic acid, can
never be easily and accurately determined. The silicates,
that undergo decomposition in acids are never so hard as to
require to be first elutriated; this operation, too, must be
avoided in order not to have to dry the powder at a higher

temperature, by which it easily parts with the water in chemical combination with it, and becomes more difficult of decomposition in acids,

Drying.—Since all impalpable powders attract moisture from the air, it is necessary to dry the powdered silicate. This is effected quite easily by placing it a short time in a moderately warm place, as for instance, in the drying chamber of a stove, previous to weighing it. A method just as good, and in many respects better, is to dry it in the desiccator a few hours over sulphuric acid.

Decomposition by Acid.—Concentrated hydrochloric acid is always employed for this purpose. (If the silicates contain much oxide of lead, it becomes necessary to use nitric acid.) The powder is first weighed in a platinum crucible (in general from one to two grammes is the quantity operated upon); this is then placed in a deep dish (not with a flat bottom), a platinum one is the best; it is then covered with a little water and intimately mixed with it by means of a glass rod, to which hydrochloric acid is now added. The dish is now heated over the flame of a lamp, taking care to stir the mixture quickly all the time, and to leave no part of the powder on the bottom of the dish unstirred. If the decomposition of the silicate is easily effected, the gritty sound of the powder, as the glass rod moves over it, soon ceases, the silicic acid separates, and the whole gelatinizes in many cases (either immediately or on cooling), and the decomposition is complete. But if the silicate is not so easy of decomposition, or if the powder is not uniformly impalpable, the heat must be continued to incipient boiling. But in every case now the decomposition must be complete. By proceeding in this way the silicic acid is prevented from aggregating around undecomposed portions of the silicate; if this is not obviated, it is not possible to produce a perfect decomposition of the silicate. The mixture is now evaporated to perfect dryness on the water-bath, stirring it well towards the last

*Frequently foreign substances in admixture remain undissolved, causing the grittiness still to continue.

in order to disintegrate the rougher portions. If the silicate contains neither alumina nor oxide of iron, the drying can be completed over the lamp, still this must be done with great care and only at a very gentle heat. In all cases, as soon as the residue is cold, it is moistened uniformly with hydrochloric acid; the dish is then covered with a plate of glass and set aside for at least an hour. Water is then added; the mixture is heated; after which the silicic acid is removed by filtration, washed with hot water, exceedingly well dried and then ignited.

Of course the filter is also ignited together with the silicic acid in the crucible, both being covered up and gradually heated; as soon as the filter is perfectly carbonized, the lid is pushed half on one side, and by means of a strip of platinum a draft is instituted and the carbon is burnt up. If the filter were to be heated in the open air, the gases and the draft produced by the lamp would carry off a considerable amount of the acid in fine dust into the air. As soon as the crucible, covered up tight, has cooled, it is weighed immediately; or the crucible is set aside to cool in the desiccator over sulphuric acid, before it is weighed; for silicic acid after ignition is exceedingly hygroscopic.

Purity of the Silicic Acid.—We have already called attention to the circumstance (vide page 141), that the silicic acid obtained in this manner is not pure, but that it contains a smaller or a larger amount of the remaining constituents of the silicate. Although in most cases the quantity of this admixture is only trifling, it is permitted only in analysis, whose aim is more technical than scientific, to regard the silicic acid at once as sufficiently pure; in all other cases it is necessary to examine the silicious residue still further, which, as already mentioned, essentially can take place by three methods, each possessing its own peculiar advantages:

1. *By Ignition with Carbonate of Soda.*—To the silicic acid in the platinum crucible are added gradually three times its weight of finely powdered dried carbonate of soda, rubbing

the mixture as intimately together as possible by means of a glass rod, and placing the crucible during the operation on a sheet of paper in order to avoid all loss; the glass tube, also, is cleaned from all adhering particles by means of a feather or camel's hair pencil. The mixture is then heated to intense ignition over the lamp or in a blast furnace; the cold mass is then detached from the crucible by slightly pressing the sides of the crucible, and placed in a beaker glass, over which is poured a sufficient quantity of dilute hydrochloric acid so as to cover it; hydrochloric acid is also poured into the crucible in order to dissolve any adhering portions; this solution is poured to the rest in the crucible which is now covered up with a concave piece of glass. The mixture is digested, and acid is added in drops as long as there is any effervescence; in this way the digestion is continued until the separate pieces of the mass have become totally decomposed into light transparent flakes of silicic acid. The mixture is now poured into an evaporating dish and so long evaporated either by continual stirring, or still more safely on the water bath until there is no longer the slightest moisture, but on the contrary the whole appears to be a dry powder. After the powder is cool, it is uniformly made moist with a few drops of hydrochloric acid and set aside for an hour; water is then added, after which the silicic acid is removed by filtration; so obtained the silicic acid is quite pure. After washing, drying and igniting it is weighed; and from its weight we shall be enabled to determine whether small portions of the bases had before been present or not. If the weight is now less than it was before, this indicates that the silicic acid had been mixed with these bases, which have now to be removed from the acid solution in the following manner, that is to say, sesquioxide of iron and alumina by ammonia, lime by oxalic acid, and magnesia by phosphate of soda, proceeding as more fully explained in their determination in the following examples.

If now, after one or more of these bases have been found

and estimated, there should still be a small quantity to be accounted for in reference to the original weight of the silicic acid, this can only consist of an alkali, which can not be sought for by this method. But such an event is of rare occurrence; and the amount of alkali in silicic acid especially is always very small, generally amounting to less in the whole silicate itself than the remaining constituents.

2. *By Boiling with a solution of Carbonate of Soda.*

From the fact, that the silicic acid obtained from the decomposition of silicates is amorphous and also after ignition is soluble in solutions of the alkaline carbonates, we have here a means for testing its purity. About 30 to 50 grammes of crystallized carbonate of soda are dissolved in a deep dish, preferably of platinum or silver, in a small quantity of water, so as to obtain a moderately concentrated solution, which is then raised to the boiling point; a small quantity of silicic acid, previously reduced to an impalpable powder in an agate mortar, is taken up on the point of a small spatula and thrown into the boiling solution; the boiling is continued until the silicic acid is dissolved; a fresh quantity is now added and so on repeatedly until the whole has been thrown in. The fluid is now quite concentrated by boiling, after which it is diluted with water, again made to boil for a moment and immediately poured upon a thin filter, which allows the fluid to pass quickly through it; any residue, that may be left on the filter, is washed with boiling water. If the amount of silicic acid had been pretty considerable, or that of the carbonate of soda not in sufficient quantity, or if the filtration should proceed slowly thus allowing the fluid to get cool, it frequently happens that the silicic acid separates in the gelatinous form; this must be avoided. The insoluble residue is ignited and weighed. The nature of this has already (vide page 143) been described in detail.

3. *By Hydrofluoric Acid.*—This is the best method by which all admixtures of silicic acid admit of being easily recognized; to this we have already alluded (vide page 144).

Estimation of the Water.—This requires a special analysis and in general is a work of no difficulty. The best plan is to break the material up into small pieces or into a sort of rough powder, since if it were in the form of fine powder, it would be apt to be carried off in the operation. The ignition is effected in closed platinum crucibles, it is continued for about a quarter of an hour and may be repeated after weighing, in order to be quite certain that every trace of water has been removed.

We will now give by examples in the following articles the analytical mode of proceeding in each of the more frequently occurring cases, presupposing an acquaintance with the general rules that have just been evolved and which may be applied to all of them.

1. SILICATE of Sesquioxide and Protoxide of IRON, sometimes with traces of Manganese, Lime and Magnesia.

(SLAGS in the refining of metals, FORGE SLAGS, STEEL SLAGS, &c.)

The powdered substance is decomposed by hydrochloric acid in the manner already given (vide page 147). The silicic acid separates in the gelatinous form. The fluid portion is filtered into a beaker glass, and is then heated; in this condition small portions of chlorate of potassa are added gradually until the smell of chlorine begins to be very distinct; by this mode of proceeding the protoxide of iron is converted into the sesquioxide. As soon as it is cold, ammonia is added gradually, stirring the mixture all the while, until an alkaline reaction becomes manifest, and the smell of ammonia begins to predominate. The sesquioxide, thus thrown down, is separated by filtration, thoroughly washed, dried, ignited and weighed. From this weight the amount of iron is computed.

Sometimes the substance contains only in addition very small quantities of lime and magnesia. To search for these and to estimate their amount the filtrate from the sesquioxide

of iron is decomposed with a small quantity of oxalic acid and then set aside for twenty-four hours. If by this time a small quantity of lime has been precipitated, it is removed by filtration, washed, dried, intensely heated, until all the carbonic acid has been expelled, which is easily effected when the quantity is small, and finally weighed as pure lime. The filtrate is mixed with phosphate of soda and also set aside for the same length of time as the precipitate. Whatever amount of the double phosphate of magnesia and ammonia is thus separated, it is treated as prescribed, page 133.

If there is only a trace of manganese, it will be found with the iron. When larger quantities are present the separation of the sesquioxide of iron, the protoxide of manganese, the lime and the magnesia must be effected in the manner prescribed, page 134.

In order to determine the relative proportion of the two oxides of iron, another portion of the substance is dissolved in a small flask with hydrochloric acid in a close vessel; the dissolved mass is then diluted with water and submitted to the volumetric process with permanganate of potassa (vide page 71). By this means the amount of protoxide of iron is obtained; and if the amount be computed as sesquioxide of iron and deducted from the total amount obtained before, we get the quantity of sesquioxide of iron in the silicate.

2. SILICATE of ALUMINA, LIME, SODA, POTASSA and WATER.

(ANALCIME, MESOTYPE, STILBITE, HEULANDITE, CHABASITE, THOMSONITE, &c.)

The amount of water is determined by ignition.

The substance in fine powder, but not ignited, is decomposed by hydrochloric acid as indicated on page 147; the silicic acid is removed by filtration, and further examined according to instructions found on page 150.

The acid filtrate is supersaturated with ammonia. This precipitates the alumina, which must be filtered off as quick-

ly as possible in a closed filter, because the fluid attracts carbonic acid, and carbonate of lime is precipitated. (If such an occurrence should happen owing to the exceedingly slow filtration, the filter together with the alumina, and without any previous washing, is placed in a beaker glass and digested with the requisite amount of dilute hydrochloric acid; the filter is then taken out, well rinsed with water, and the alumina is precipitated as before with ammonia.) The alumina is thoroughly washed with boiling water, until a drop of the filtrate when evaporated on platinum foil scarcely leaves any mark behind. As soon as the substance has been dried in the air, it is ignited and weighed,

Since the fluid, from which the alumina has been precipitated, attracts carbonic acid from the atmosphere, thus giving rise to a separation of carbonate of lime only when it contains *free* ammonia, this may be avoided by boiling the mixture as soon as the ammonia has been added, until all smell of the latter has been expelled. If already some carbonate of lime had been formed, it would be decomposed by the chloride of ammonium present, and the lime would again be dissolved. The alumina is removed by filtration whilst the fluid is still hot; but the washing must not be continued too long as the residue is apt to clog the pores of the filter. On this account the substance is allowed to dry, until it cracks up into separate parts, which however are still moist in the inside, and the washing with hot water is completed.

Oxalic acid, quite free from any admixture of alkali, is added to the filtrate. (The solution of oxalic acid must leave no residue when heated in a platinum crucible.) By this means the lime is precipitated, but completely only when the fluid has an alkaline reaction, and has been set aside for at least twelve hours after the addition of oxalic acid. The oxalate of lime is collected on a filter, then washed with hot water, dried and converted into carbonate of lime according to the rules laid down on page 132.

The filtrate is evaporated to dryness, towards the last in a

water-bath; the residue is carefully removed from the dish and placed in a platinum crucible loosely covered; it is then heated as long as ammoniacal vapors are given off; afterwards a few drops of hydrochloric acid are added so as to moisten it thoroughly; the lid is now firmly closed, and the mass is again heated, and towards the last gently ignited. Intense ignition, but especially opening of the crucible during this operation, is apt to produce a loss of alkaline chloride. After cooling, the residue is immediately weighed; it consists of a mixture of chloride of potassium and of chloride of sodium. Whilst still in the crucible it is covered with water and heated; this dissolves all, with the exception of a few flakes of silicic acid, which is removed by filtration on a small filter, washed, dried and ignited. This weight is added to that previously received, but deducted from that of the chlorides. The fluid portion, which had been received in a dish, is mixed with a sufficient quantity of a solution of chloride of platinum so as to convert the chlorides into double chlorides, and evaporated on the water-bath almost to dryness. The residue, whilst still moist, is allowed to cool, and is then mixed with moderately strong alcohol (spec. grav. 0.83), containing from one-sixth to one-fifth its volume of ether; the precipitated double chloride of platinum and potassium is separated by filtration on a filter, previously dried at a temperature of 248°F. and weighed, it is then washed with the mixed alcohol and ether, and dried, towards the last at a temperature from 248°F. to 256°F. until its weight remains constant.

The amount of chloride of potassium is computed from the weight of the double chloride of platinum and potassium; this is next deducted from the total weight of the two chlorides; the difference is the weight of the chlorides of sodium. The respective amounts of potassa and soda are easily computed from those of their chlorides.

If it be desired to make a direct determination of the amount of soda, an operation which is less accurate, but still

all right and proper in order to be convinced of its presence and to test its purity, a concentrated solution of chloride of ammonium is added to the alcoholic fluid to precipitate the largest proportion of the platinum in excess. The double chloride of platinum and ammonium is received on a filter and washed with dilute alcohol. The filtrate is evaporated to dryness in a dish; the residue is then placed in a porcelain crucible and heated until the ammoniacal salt is volatilized; as soon as it is cold, it is moistened with a solution of oxalic acid and evaporated to dryness. The dry mass is heated to a high temperature, and afterwards the chloride of sodium is dissolved leaving the reduced platinum undissolved.

In order to ascertain whether the double chloride of platinum and potassium is pure, it is folded up in the filter and moderately heated in a porcelain crucible in order to carbonize the filter. Hydrogen gas is then introduced, while the salt is being heated, finally to ignition. Water dissolves the chloride of potassium leaving the platinum undissolved, which is then weighed. Its amount must be forty and one-half per cent of the double salt. Furthermore the solution of the chloride of potassium can easily be tested as to the absence of soda.

On the other hand the purity of the chloride of sodium and especially its freedom from chloride of potassium may be ascertained by evaporating its solution when mixed with sulphuric acid in a platinum crucible to dryness; the dry mass is intensely heated, and afterwards dissolved in water. This solution is placed on a watch glass and set aside to evaporate spontaneously. As soon as the fluid has dried, the crystals of the sulphate of soda soon begin to effloresce, and may be with care blown off, whilst, if there be any potassa, it may be easily distinguished by the presence of hard and transparent crystals of sulphate of potassa which may be furthermore recognized by their shape.

OBSERVATION.—In the analysis of silicates containing alkalies there are generally found in the chloride of sodium very minute quantities of alumina, lime, or magnesia.

which in accurate operations have to be determined.

3. SILICATE of Protoxide of IRON, Protoxide of MANGANESE, ALUMINA, LIME and MAGNESIA.

(SEVERAL SLAGS.)

The substance, reduced to a fine powder, is decomposed by means of hydrochloric acid, and silicic acid separates.

If the amount of manganese is small, the process for the separation of the bases is that found on page 127, that is, the solution is mixed with chloride of ammonium, then ammonia is added in excess, and the mixture is then boiled, &c. The small quantity of manganese then remains in the oxide of iron.

If the sesquioxide of iron and alumina are to be determined by a direct process, the ignited and weighed precipitate of the two in mixture is reduced in an agate mortar to an impalpable powder, and then all that can be shaken out of the mortar is again ignited and weighed. (Since this is not the entire original quantity, from the fact that a portion is lost, the final results are computed in reference to the original quantity.) This is rubbed up in a silver crucible together with a small quantity of carbonate of soda, pure hydrate of potassa is then added in sufficient quantity; the covered crucible is then heated very cautiously (on account of the incipient foaming) over the lamp. Finally the temperature of the melted mass is raised to ignition, and maintained at this heat for about a quarter of an hour. As soon as the crucible is cold, it is placed in water, to which (for the reduction of the manganic acid) a small quantity of alcohol is added; the mixture is now heated to boiling, filtered and washed with hot water. The residue on the filter, consisting of sesquioxide of iron, is digested, together with the filter, in hydrochloric acid; the solution is diluted and filtered; and the oxide of iron is precipitated with ammonia. The solution of the alumina in potassa is slightly acidified with hydrochloric acid (taking care that nothing is lost by the effervescence of

the fluid), and then sulphide of ammonium is added; this precipitates the alumina, which is washed with hot water, dried, ignited and weighed. The sum of the weight of this and of that of the sesquioxide of iron must correspond to the amount of the precipitate used in this experiment.

OBSERVATION.—If the hydrate of potassa, as is so frequently the case, is not quite free from silicic acid and alumina, the direct determination of the alumina in the solution of potassa is omitted, and its amount is obtained by taking the difference.

If the amount of the manganese is more considerable, perhaps greater than that of the iron, as for instance in many slags from the smelting furnaces, the process is as follows: to the fluid filtrate from the silicic acid chloride of ammonium and a small quantity of acetate of soda are added; the mixture is then heated and a current of chlorine is passed through it to saturation; ammonia is added and afterwards the whole is boiled in order to expel all the free ammonia. The precipitate, consisting of sesquioxide of iron, binoxide of manganese and alumina, is separated by filtration and thoroughly washed with hot water; it is then dissolved in hydrochloric acid, to which a small quantity of alcohol is added, the solution is diluted, but not filtered, and then carbonate of baryta levigated with water is added in sufficient quantity so as to leave a slight excess undissolved. The mixture is now set aside for about an hour, being frequently stirred up during the time. The sesquioxide of iron and the alumina, together with the carbonate of baryta in excess, are now removed by filtration, washed with cold water, and dissolved in dilute hydrochloric acid; sulphuric acid throws down the baryta, which is left by filtration on the filter; sesquioxide of iron and the alumina are precipitated by ammonia; after ignition and weighing, these substances are separated as before indicated. The fluid, containing manganese, is treated in like manner with sulphuric acid which removes the dissolved baryta, afterwards with carbonate of soda and boiled (vide page 67); and in this way the manganese is estimated.

From the filtrates of the three bases lime is thrown down by oxalic acid, and magnesia by phosphate of soda according

to methods already given.

OBSERVATION.—Small quantities of sulphur in the form of metallic sulphides, as also of the alkali, are found in several slags. The first is recognized during the decomposition of the silicate by the evolution of hydrosulphuric acid. To estimate its amount, a separate quantity of the fine powder is mixed in a small flask with chlorate of potassa and a small quantity of water; hydrochloric acid is added to the mixture, which is digested until the sulphur is converted into sulphuric acid; the mixture is then diluted and submitted to filtration, which removes the silicic acid; the sulphuric acid is then determined by means of chloride of barium. The amount of sulphur is computed from the sulphate of baryta.

In order to determine the amount of potassa or soda the process, previously given, is followed, excepting that acetate of soda is left out; and, after the separation of the lime, the magnesia is separated from the alkali by means of hydrate of baryta, or carbonate of ammonia as will be shown further on (vide: Silicates that are not decomposable by acids and which contain magnesia and alumina).

4. SILICATE of the Protoxide of IRON, ALUMINA, LIME and MAGNESIA, with small quantities of oxide of LEAD or of COPPER.

(LEAD OR COPPER SLAGS.)

The substance is decomposed by hydrochloric acid according to the general rules already given (vide page 147). If lead is one of the constituents, the silicic acid must be carefully washed with boiling water, in order that no chloride of lead may remain mixed up with it.

A current of hydrosulphuric acid is passed through the filtrate in order to precipitate the lead or copper; as soon as the precipitate is complete, the residue is filtered off as quickly as possible in a covered funnel to prevent all access of air; the filtrate is received in a dish.

If the precipitate consists of lead, it is treated as directed on page 61. If on the contrary it consists of sulphide of copper and its amount is very small, it is raised to intense ignition in a current of air; by this means it is converted into the oxide of copper which is weighed. When the amount is large, it is treated, on the contrary, according to the method given on page 52.

The filtrate from the metallic sulphide is concentrated to a small volume by evaporation, it is then oxidized by chlorate of potassa and diluted; from the dilute solution the bases are separated as in the preceding example.

5. SILICATE of the oxide of ZINC with Water.

(CALAMINE OR SILICIOUS OXIDE OF ZINC.)

Although pure calamine is nothing more than a hydrated silicate of the oxide of zinc, yet it occurs generally accompanied with zinc spar (carbonate of the oxide of zinc), brown hematite (hydrated oxide of iron) and limestone, &c. Galmei is frequently thus constituted, from which zinc is extracted. The substance therefore contains oxide of zinc, oxide of iron, lime, magnesia,* silicic acid and water.

A quantity of the substance (sufficient for all the experiments) is reduced to an impalpable powder.

a)—In one part the amount of carbonic acid is determined according to the method given on page 129.

b)—Another portion is decomposed by hydrochloric acid. The silicic acid is removed by filtration and tested as to its purity; the filtrate is diluted, moderately warmed, and then carbonate of soda is added until the fluid begins to assume a dark-red color, or in fact until a portion of the basic salt of the oxide of iron is precipitated, whereupon acetate of soda is added and the mixture is made to boil. By this means the sesquioxide of iron is separated from the oxide of zinc and earths here present as also from the protoxide of manganese and the oxides of copper and cobalt. (Compare pages 67 and 133.)

A current of hydrosulphuric acid is passed through the filtrate from the sesquioxide of iron (the filtrate must contain a sufficient quantity of acetate of soda). This precipitates the zinc. The sulphide of zinc is allowed to settle completely, it is then filtered in a covered funnel as quickly as possible, washed with water containing in solution hydrosulphuric acid, and digested with hydrochloric acid. The solution is diluted and raised to a boiling temperature; carbonate of soda is then added, and the mixture is filtered; the residue is washed, dried and ignited.

The filtrate from the sulphide of zinc is freed from hydro-

*Contained in dolomitic limestone.

sulphuric acid by heating; ammonia is then added in excess, and afterwards oxalic acid (vide page 131). After the removal of the oxalate of lime by filtration, the magnesia is precipitated by phosphate of soda (vide page 133).

c)—The amount of water in the substance is computed either from the loss, or by igniting a separate portion intensely, which drives off at the same time both the water and the carbonic acid, and then by deducting the amount of the latter (found in a) from the loss thus produced by heat.

6. SILICATE of ALUMINA and SODA, containing SULPHIDE of SODIUM.

(ULTRAMARINE, LAPIS LAZULI, HAUYNE, &c.)

Ultramarine contains, besides a silicate of alumina and soda, one or more sulphides, whose nature is not yet accurately known, nor can they be determined by the analysis, for this is limited to finding the amount of sulphur. In general also are found small quantities of lime, potassa, chlorine and sulphuric acid.

A.—The substance, previously reduced to a fine powder, is decomposed by hydrochloric acid. By this treatment it loses its color, evolves hydrosulphuric acid and forms a complete gelatinous substance. After evaporation, &c., the silicic acid is separated, dried, ignited and weighed. It was accompanied with sulphur, which volatilized when heated. It is tested in reference to its purity (vide page 148).

Chloride of barium is added to the filtrate as long as sulphate of baryta is precipitated, which is allowed to settle, then filtered, thoroughly washed and ignited. From its weight the amount of sulphuric acid may be computed.

Dilute sulphuric acid is cautiously added to the filtrate in order to throw down all excess of chloride of barium; after which the alumina is precipitated by ammonia. The precipitate is washed with hot water, dried, ignited and weighed. (The alumina frequently contains a small quantity of oxide of iron.)

Oxalic acid (free from alkali) is added in small quantity to the filtrate from the preceding precipitate, in order to precipitate the lime, proceeding in this respect as directed on page 132.

After this the fluid is evaporated to dryness; the residue is placed in a platinum crucible, heated but not to ignition, until all vapors from ammonical salts have passed off, it is then intensely ignited, thus converting the sulphate of soda (and sulphate of potassa) by the method given in detail on page 113 into neutral sulphate, which is weighed.

If it be desirable to determine the small amount of potassa which is frequently contained in the residue, the sulphates must first be converted into chlorides. This is effected by mixing them in a porcelain crucible with chloride of ammonium, and heating the mixture as long as any vapors of ammoniacal salts are given off, taking care that the temperature is not so high as to fuse the mass. This treatment with chloride of ammonium must be repeated until the weight of the residue remains constant. The chlorides thus produced are separated by means of the chloride of platinum according to the rules given on page 154.

B.—In order to determine the whole amount of sulphur, the process to be followed will be found on page 158, taking care that no part of the sulphur remains unoxidized. Instead of filtering immediately after the solution is diluted, the whole may be evaporated to dryness, then treated with water and filtered; to the filtrate add hydrochloric acid and afterwards chloride of barium. If the sulphur be computed from the amount of sulphate of baryta, that portion must be deducted which is contained in the sulphuric acid found under article A.

As regards the analysis it is a matter of indifference, but as regards the constitution of the ultramarine and similar bodies it is interesting to determine how much sulphur is set free by decomposition by means of hydrochloric acid and how much in the form of hydrosulphuric acid. For this pur-

pose therefore a fresh quantity is dissolved by acid, the gelatinous silicic acid, together with the sulphur, is removed by filtration, thoroughly washed, dried and then treated with chlorate of potassa and hydrochloric acid. As soon as the sulphur has been completely oxidized, the solution is diluted and filtered, after which the sulphuric acid thus produced is precipitated by chloride of barium. By deducting the amount of sulphur, computed from the sulphate of baryta, from the total weight of the substance, we obtain that part which is evolved in the form of hydrosulphuric acid.

C.—In order to estimate the amount of chlorine, a separate quantity of the substance is treated with nitric acid at a very gentle temperature; the silicic acid is removed by filtration; to the filtrate nitrate of silver is added to precipitate the chlorine. If the chloride of silver should contain any sulphide of silver, it is separated after drying and weighing by digestion with ammonia.

Here also the bases, which generally occur, are the same which are met with in the silicates that can be decomposed by acids (vide page 145), namely: the oxides of iron and manganese, magnesia, lime, soda and potassa. Of those which occur less frequently we find the following:

LITHIA (Petalite, Spodumene, Mica, Tourmaline.)

BARYTA (Felspar.)

GLUCINA (Beryl and Emerald, Phenakite, Euclase, Chrysoberyl, Leucophane.)

OXIDE OF ZINC	} Slags and Glasses ;	
„ „ LEAD		small quantities
„ „ COPPER		in some minerals.

OXIDE OF NICKEL (Pimelite, Saccharite, Chrysoprase, Olivine.)

OXIDE OF COBALT (Smalt.)

OXIDE OF CHROMIUM (Chrome ochre, Garnet, Pyrope, Serpentine, Miloschine, Chrome Mica, &c.)

Of electronegative bodies are the following:

Stannic acid (Glasses and Enamels.)

Titannic acid (Acmite, Several sorts of Mica, Hornblende, &c.)

ZIRCONIC ACID (Zircon.)

BORACIC ACID (Axinite, Tourmaline, Several Glasses and Enamels.)

PHOSPHORIC ACID (Sordawalite, Mica.)

FLUORINE (Topaz, Leucophane, Mica, Hornblende, Scapolite, Slags, &c.)

Water is sometimes a constituent of this class of silicates.

Judging from the number, this division is the larger of the two; and we find in it not only the most important and the most widely scattered minerals, such as felspar, mica, hornblende, augite, garnet, tourmaline, &c., but also the different sorts of glass.

In order to decompose these compounds, the following methods in particular present themselves, namely:

A.—Ignition with Carbonate of Soda.

B.—Ignition with Carbonate of Lime and Chloride of Ammonium.

C.—Solution in Hydrochloric acid.

D.—Decomposition by means of Sulphuric Acid.

Other methods, for instance the application of carbonate of baryta, of caustic potassa, or of fluor spar and sulphuric acid, are scarcely any longer made in reference to the analysis of silicates. The first mentioned is used, however, in the following way: Decomposition by means of carbonate of soda, a process which is most frequently employed, serves to determine all the constituents of a silicate with the exception of the alkalies; if these are absent, this method naturally completes the analysis. The use of carbonate of lime and chloride of ammonium is sufficient for the determination of all the constituents of a silicate, even of the alkalies; whilst by means of hydrochloric acid all the constituents, with the exception of silicic acid, may be determined.

A complete description of these processes, together with examples for each, will be found in the following articles.

A. ANALYSIS of SILICATES with CARBONATE of SODA.

If a silicate, which is decomposed by an acid with difficulty or not at all, is ignited with carbonate of soda, carbonic acid is evolved, with the formation of silicate of soda at the expense of a part of the acid taken from the bases, thus giving rise to a mixture or a combination of basic salts, that can easily be decomposed by a strong acid. The efficacy of carbonate of soda consists therefore essentially in the conversion of silicates of this class into those of the former, consequently the further steps to be taken in the analysis are in fact precisely similar to those already described.

GENERAL RULES for the ANALYSIS.

Pulverization. We have already remarked, that this operation must be carefully performed, and that those silicates, that are very rare and that can with difficulty be decomposed, must be subjected also to elutriation. (Compare page 146.)

Drying and Weighing of the Substance.—The impalpable powder must first of all, in all accurate investigations, be dried. If the substance contains water, it is ignited at a low temperature in a covered platinum crucible and weighed. If, on the contrary, we have to deal with a hydrated silicate, the drying of the powder must be effected in the drying chamber of a common stove, or in the drying apparatus at a temperature of between 86°F. and 104°F., or in the desiccator over sulphuric acid.

OBSERVATION.—With some porous silicates it is very difficult to determine how much hygrometric water and how much water in chemical combination they contain, since a portion of the latter appears to be given off by a gentle heat also over sulphuric acid, in the same manner as several crystallized salts effloresce under similar circumstances owing to the loss of their water of crystallization.

The powder, having been dried and weighed in a small platinum crucible, is shaken into a more capacious crucible; the small crucible, together with any adhering powder, is again weighed in order to ascertain with accuracy the quantity of powder about to be used in the analysis.

Admixture with Carbonate of soda.—Dry carbonate of soda, to the amount of the substance, is taken and rubbed to a fine powder in an agate mortar; the platinum crucible containing the substance to be analyzed, is then placed on a sheet of smooth paper, and about half the carbonate of soda is poured into the crucible and, by means of a glass rod with a smooth round end, the two substances are intimately mixed together until they form one homogeneous substance. More carbonate of soda is now added and again mixed as before, and so on until nearly all the soda has been poured in. Finally the glass rod is brushed thoroughly clean with a feather, and the remaining part of the soda is poured into the crucible and is allowed to form a layer to cover the rest.

Ignition.—This operation is performed either in the blast furnace or over the lamp according as the quantity of the mixture is large or small. When a silicate is ignited with carbonate of soda, the mass is either completely *fused* or has only undergone a sort of semi-fusion. In order to obtain a perfect decomposition, fusion is by far to be preferred; but all silicates rich in alumina and magnesia, as a general thing, can be reduced only to a semi-fused mass. On this account it is necessary in these cases, that the powder used for the analysis should be exceedingly fine, even sometimes elutriated; whilst in those cases where the fusion is complete, this is not necessary to the same extent, since in the melted fluid mass all the parts come in contact with each other.

If a blast furnace be used, the platinum crucible well covered up is placed in a Hessian or French crucible, which is also covered, and at the bottom of which had been previously placed a layer of either calcined magnesia or its carbonate, in this the platinum crucible is embedded and prevented from coming in contact with the sides of the greater crucible.

The ignition in all cases must be maintained for at least half an hour, reckoning from the time when the mass had attained the temperature of ignition.

Decomposition of the Ignited Mass by Hydrochloric Acid.

As soon as the crucible is cold, the melted mass is loosened from the sides of the crucible by gentle pressure and then transferred to a beaker glass. This transference is sometimes quite complete, especially if the mixture has undergone only a sort of semi-fusion. If some parts, however, adhere firmly to the crucible, water is poured upon them and heat applied; and if this does not effect their complete separation a few drops of hydrochloric acid are added, and the crucible is covered up and set aside for some time. If, however, the fused contents of the crucible adhere so firmly as scarcely to be affected by pressure, then the crucible itself together with the cover (if any of the fused substance adheres to it) is placed in the beaker glass and digested with the dilute acid, re-collecting, however, that, if the mass has a green color and consequently contains manganic acid, chlorine will be set free and will act upon the crucible itself (vide page 37). In such a case as this alcohol is first put in the crucible before the acid comes in contact with the platinum.

The mass in the beaker glass is well covered with water, the beaker glass being furnished with a concave plate of glass as a cover; hydrochloric acid is then added gradually and cautiously, in order that nothing may be lost by effervescence.

The fluids, that were used for cleaning the crucible, are likewise added either now or later. The mixture is now digested either on the sandbath, in the digestorium or in fact in any moderately warm place, taking care to break up the larger pieces by means of a glass rod, because they easily become covered with the silicic acid as it separates and are thus protected from the action of the decomposing agent. In case of need also more acid is added. The silicic acid must separate in the form of light flakes (sometimes the whole becomes a gelatinous mass), and when the digestion is finished and the glass rod is rubbed over the bottom of the glass no hard sandy particles must be observed producing a gritty sound.*

*It is necessary to guard against being deceived, for, when the fluid is highly concentrated, crystals of chloride of sodium are easily formed; but these dissolve immediately on the addition of hot water.

Although now the largest portion of the silicic acid has separated, no inconsiderable portion remains dissolved in the fluid, which has to be converted into the insoluble form by evaporation. To effect this the whole is placed in a moderately deep dish (a platinum dish is the best), and is concentrated by evaporation and constant stirring to dryness. Since, however, the thick fluid is very apt to bubble up and spirt, it is by far the best to evaporate it on the water-bath, continually stirring the mixture in order to break up the incrustation of chloride of sodium, which forms on its surface, for this prevents the vapors from passing off. The evaporation is continued, until the mass has assumed a dry dusty appearance, when the vessel may be placed over an open fire, or over the flame of a lamp for a few minutes, constantly stirring the mixture, taking care, however, with silicates rich in iron not to raise the temperature so high as to separate some of the oxide of iron, which manifests itself by communicating a red color to the mixture; for if this should take place, the oxide is not again dissolved by the acid, and consequently remains with the silicic acid.

Towards the end of the evaporation the weaker bases, such as sesquioxide of iron and alumina, have lost a portion of their hydrochloric acid, and, if the mass were treated immediately with water in order to remove all that is soluble, a part of these bases would remain insoluble with the silicic acid. Therefore in order to reinstate that portion of acid which has been volatilized, the mass, as soon as it has cooled, is moistened uniformly with a few drops of hydrochloric acid and set aside for at least half an hour. Water is then added and the mixture is placed on a filter; after which the silicic acid is thoroughly washed with boiling water, and afterwards dried spontaneously; it is then ignited and weighed. The precautionary measures recommended in regard to this ignition on page 148, are to be observed here.

In the acid filtrate are found all the bases contained in the silicate, and these have to be separated by means described

in the following example. This fluid contains also still a small quantity of silicic acid, which is precipitated at the same time with the bases, but the difficulty of its separation from these is in some measure very great, and its amount so minute as not to make any essential change in the result as a general thing. At the very most it might be advisable to eliminate that portion which remains in solution in the fluid after the bases have been precipitated. The filtrate then is evaporated to dryness; and water is added to dissolve what is soluble; after which the small quantity of silicic acid is left behind.

The silicic acid is pure, if the decomposition is complete. It is customary to test it, as to its purity, by projecting it in small quantities at a time into a boiling concentrated solution of carbonate of soda (vide page 149).

In general it is the custom to regard the undissolved portion as undecomposed material and to deduct it both from the amount of the original quantity started with and from that of the silicic acid; there might be just as little propriety in doing this here as with those silicates which are soluble (vide page 142), for the residue consists, as experience has taught us, of silicic acid and a variable amount of certain bases, as for instance, alumina and magnesia; and such silicic acid not altogether quite pure is what is received by the observance of all the precautionary measures of analysis, that is, even when the powder was quite impalpable, and the fusion and decomposition of the fused mass had been quite complete. This occurs especially: firstly, with silicates which contain more than fifty per cent of silicic acid and are rich in magnesia, for instance with tremolite; the silicic acid in this instance always contains magnesia; secondly, with the silicates rich in alumina, and poor in silicic acid (cyanite, andalusite, staurolite); in this case the silicic acid always contains alumina.

If the amount of the residue from the solution in carbonate of soda is very small, it is best to regard it as silicic acid; if it is considerable, or if the greatest accuracy is required in the

analysis, the residue is either ignited again with carbonate of soda, &c., after which the silicic acid and the bases are estimated, or, after it has been dried and the filter has been incinerated, it is covered with hydrofluoric acid, &c. (vide page 144), or it is heated with fluoride of ammonium and sulphuric acid, by which means the bases are retained as sulphides.

In all accurate analyses, the aim of whose results is purely scientific, it is best to heat right away the ignited and weighed silicic acid with hydrofluoric acid (or with fluoride of ammonium), finally to treat it with sulphuric acid and to continue the analysis of the remaining sulphates of alumina, sesquioxide of iron, magnesia and lime.

The great difficulty in the analysis of silicates lies in the separation of the silicic acid from the bases. If the mass, which has been decomposed by means of acid be simply evaporated to dryness on the water-bath, the silicic acid is obtained in a purer condition, but it is also in a condition to be more easily dissolved afterwards together with the bases in which it has to be sought as also in the last filtrate. But if the mass, after it has been evaporated to dryness on a water-bath, be heated over an open flame, the reverse takes place.

Estimation of the Water in Silicates.—This operation will be found on page 151. The ignited product, after reduction to an impalpable powder, may afterwards be employed for the subsequent analysis, in case there is a lack of material. If the silicate contains protoxide of iron, it will be oxidized by ignition, and consequently an anhydrous silicate of this nature when ignited will increase in weight. With hydrated silicates, therefore, the amount of water is obtained by adding to the loss incurred by ignition the amount of oxygen which was necessary to convert the protoxide into sesquioxide of iron. In such cases the color of the silicate is generally changed into a yellow or reddish.

The operations just described are those to be followed in the analysis of every single silicate, so that in the examples which

follow we shall take into consideration alone that which is necessary for the further determination of the bases.

1. SILICATE of LIME and MAGNESIA.

As soon as the silicic acid has been separated by the methods already given, the acid fluid is neutralized with ammonia slightly in excess; after which the lime is precipitated with oxalic acid (vide page 131), and the magnesia with phosphate of soda (vide page 133).

2. SILICATE of ALUMINA, PROTOXIDE of IRON, PROTOXIDE of MANGANESE, LIME and MAGNESIA.

The filtrate from the silicate is analyzed according to instructions on page 155.

3. SILICATE of ALUMINA and Sesquioxide of IRON together with Water. (CLAY.)

The purest specimens of clay contain besides these essential constituents small quantities of lime, magnesia and alkalis. Moreover they are frequently mixed with quartz or the remains of those minerals to the decomposition of which they owe their formation (felspar). The analysis of clay containing these admixtures, with the exception of the determination of the alkalis, is effected as in the preceding example, which consult.

4. SILICATES containing FLUORINE.

The analysis of the native silico-fluorides, given on page 263, is no easy matter; and the accurate estimation of the fluorine is scarcely possible. The different steps of the analysis are not always the same, depending as they do on the different amounts of fluorine in the substance.

As it appears the fluorine may be driven completely from the silicates by a sufficiently high temperature in the form

of fluoride of silicon; and, when the silicates contain no water, this is the simplest method of determining the amount of the fluorine; nevertheless this method can be applied with ease only to those silicates which contain but a small amount of fluorine. The ignition is best effected in double platinum crucibles, placed in Hessian, &c., crucibles, and by means of a very high temperature in a blast-furnace; by this treatment all the fluorine in micas containing but small quantities, as also in tourmalines, &c., is entirely expelled. Even from the silicates the richest in fluorine, topaz and pyknite, Forchhammer, Deville and Fouque have received, by intense ignition, residues entirely free from fluorine; but such results require the most intense white heat, to produce which the necessary means are not always on hand.*

If such a silicate (mica) contains water, which at the same time requires a high temperature for its complete expulsion, the determination of the fluorine can not be effected by ignition.

In silicates containing only minute quantities of fluorine, this substance has been frequently overlooked, and not only in those which may be decomposed by acids (apophyllite) but also in those which can not be decomposed. In the ordinary course of their analysis, there is always a corresponding loss of silicic acid which passes off as fluoride of silicon.

A.—*Analysis of silicates containing only minute quantities of Fluorine*, that is, of such as contain at most but a small percentage of fluorine. The fine powder is ignited with four times its weight of carbonate of soda, The semi-fused or completely fused mass is digested or boiled in a platinum or silver dish with water; the residue is washed with boiling water for some time (a thorough extraction by washing is impossible). The filtrate, containing in solution fluorine in the form of a fluoride of sodium, and likewise a certain amount of silicic acid and alumina is decomposed with

*Pyknite in my experiments in the blast-furnace, heated with coke, lost only fifteen per cent, that is, 10.75 of fluorine; whereas, according to Forchhammer, it must have lost 25.8 per cent, that is, 18.48 of fluorine.

solid carbonate of ammonia and warmed. By this means the alumina and part of the silicic acid are precipitated, and then removed by filtration; the filtrate is concentrated by evaporation and then neutralized as accurately as possible with nitric acid; a few drops of dilute acetic acid are added, then the mixture is evaporated to dryness on a water-bath. The dry mass is now treated with cold water, which leaves silicic acid undissolved; this is removed by filtration, after which the filtrate is again evaporated to dryness and dissolved. At this stage the fluorine is precipitated by means of a solution of chloride of calcium and by raising the mixture to boiling; the latter is then allowed to settle, and the supernatant fluid filtered. The residue is again boiled with water, and allowed to settle; the fluid is decanted and filtered; and the operation is repeated until all that is soluble in the residue in this way has been pretty thoroughly removed by washing. The latter finally is collected on the filter, dried, ignited and weighed.

Observation.—In order to determine the presence of very minute quantities of fluorine, the ignited precipitate is gently heated with a little concentrated sulphuric acid in a crucible covered with a plate of glass prepared for the purpose. As soon as the presence of fluorine is shown by the corrosion of the glass plate, the crucible is closed with its lid and heated, at last to low ignition; the sulphate of lime, thus formed, is then weighed and from its weight the purity of the fluoride of calcium is determined. (The equivalents of fluoride of calcium and of sulphate of lime have the ratio of 39 to 68 or of 1 to 1.7436.)

The first residue, as well as also those obtained from the filtrate containing fluorine, are dried, then separated from the filters and digested together with the ashes of the filters with dilute hydrochloric acid, by which the mass is gelatinized. The gelatine is evaporated to complete dryness on the water-bath, after which the silicic acid is separated according to the method found on page 167. The bases of the silicate are to be sought for in the filtrate.

B.—*Analysis of Silicates Rich in Fluorine.* If the attempt be made to determine the amount of fluorine, in the manner described, in silicates containing ten per cent of fluorine or more and at the same time not much silicic acid, the

whole amount of fluorine can not be obtained because of the want of a sufficient quantity of silicic acid. Forchhammer has shown that this defect can be remedied by the addition of more silicic acid. Therefore one part of the fine powder of the silicate is mixed with from one-half to one part of recently ignited pure silicic acid and from 4 to 6 parts of carbonate of soda. The mass is then heated, at the beginning it melts and then again concretes, after which it is raised to an intense ignition, proceeding in other respects precisely as previously described. If the amount of silicic acid had been accurately weighed, all that is needed is to deduct it from the whole amount in order to ascertain that portion contained in the silicate.

5. SILICATES containing BORACIC ACID.

(TOURMALINE, AXINITE.)

The great difficulty of the direct determination of boracic acid has hitherto been the reason of estimating its amount indirectly from the loss, after the most accurate separation of the silicic acid and the bases, as computed from their quantity. The greater the number, however, of the bases, the more complex will be the course of the analysis, and the less inevitable will be the losses; the computation, therefore, of the boracic acid will be inaccurate, especially, when besides the earths and the oxides of iron and manganese, there are present also the alkalies, as in tourmaline, whose determination requires a special analysis. The direct determination of boracic acid, however, may be effected by aid of the method given on page 136, if all the requisite precautionary measures are observed.

The substance, reduced to a fine powder, is ignited with four times its weight of pure carbonate of potassa; the mass is then ignited and boiled with water (to which alcohol is added, if the fluid becomes green by the formation of manganic acid); the mixture is then filtered, and the residue is washed for some time with hot water. The filtrate contains the bo-

racic acid as borate of potassa, and in addition a small quantity of silicic acid and alumina. In order to separate both of these, chloride of ammonium is added, and the mixture is heated for some time; the precipitate thus formed is separated by filtration; and the operation is repeated with the filtrate until there is no further separation of any thing (the fluid may also be evaporated to dryness on the water-bath), the fluid is then heated with a small quantity of carbonate of potassa in order to destroy the undecomposed chloride of ammonium, after which hydrate of potassa is added in excess. The boracic acid is now determined, according to instructions given on page 136 as borofluoride of potassium.

The residue containing the silicic acid and the bases, as well as the precipitate of silicic acid and alumina obtained afterwards, are dried and rubbed off from the filters. These are incinerated, and the ashes are added to the preceding residues, which are decomposed with dilute hydrochloric acid; in this way the silicic acid is separated from the bases, after which these are separated from one another by methods already known.

B.—*Analysis of Silicates by means of Carbonate of Lime and Chloride of Ammonium.*

This method, as well as the following for the solution of the silicates by means of hydrofluoric acid, is applied in the analysis of silicates containing the alkalies, for which purpose the preceding naturally could not be used for their determination at the same time with the rest.

The silicate is previously reduced to an impalpable powder, or even elutriated, if the decomposition is to be successful. This powder is mixed in a platinum crucible with an equal weight of ammonium and five times its weight of carbonate of lime (prepared by precipitation from pure chloride of calcium with carbonate of ammonia); the crucible is then closed and heated slowly, just raising the temperature of the bottom of the crucible to a low red heat and maintaining it so for some time. After the expiration of half an hour the

temperature is raised to intense ignition, which reduces the contents to a semi-fused condition, but does not fuse them. The process with the contents, which can easily be removed from the crucible, is the same exactly as that pursued in the fusion of a silicate by carbonate of soda (vide page 165); the silicate is first estimated, and then the bases in the filtrate, resorting partly to the methods already given (page 152), and partly to such as are described hereafter in the decomposition by means of hydrofluoric acid.

Although this method has the advantage of determining at the same time both the silicic acid and the alkalies, it is subject for all that to some disadvantages. The great amount of lime, which thus enters the analysis and which has to be separated before we can search for the bases, entails a very considerable amount of precipitate of oxalate of lime. If the silicate itself also contains lime, the amount of carbonate of lime added, which must be well dried, must be accurately weighed; and the conversion of the oxalate of lime, obtained afterwards, into carbonate of lime, as also the operation of weighing it, in order to obtain the amount of lime in the silicate by deducting this weight, is on account of its large amount a difficult piece of work.

Furthermore the silicic acid, after it has been weighed, has to be tested as to its purity; and if, after it has been boiled with a solution of carbonate of soda (vide page 150), it should leave a residue, this has to be deducted without any more to do as undecomposed substance, which possibly may give a false result.

C.—*Analysis of Silicates with Hydrofluoric Acid.*

There is no method for the accurate determination of the alkalies and the remaining bases in silicates equal to this one first introduced into analytical chemistry by Berzelius. It is founded upon the fact, that when a silicate is heated with hydrofluoric acid, the silicic acid is partly volatilized as fluoride of silicon, and the bases are converted into silico-fluorides. Adding sulphuric acid at the same time, the silico-fluorides

lose all the fluoride of silicon and pass into sulphates, whose bases then admit of being separated.

Since, however, when a silicate is decomposed by hydrofluoric acid the amount of silicic acid is not found by a direct method, this determination is used only in those cases where a deficiency of material precludes the special determination of silicic acid. In all other cases a separate quantity of silicate is fused with carbonate of soda, in order to compare the quantity of silicic acid got by this process with that from the solution with hydrofluoric acid, which to be correct must be equal (not comprehending in the loss the water or other volatile or undetermined constituents such as fluorine or boric acid). Besides it is always highly to be recommended not to confine the analysis with carbonate of soda to the determination of silicic acid, but to extend it to the determination of all bases, excepting of course the alkalies, so that the two analyses in this respect may be a check on one another.

The different silicates are not decomposed by hydrofluoric acid with equal facility; those, which in general are decomposed by acids, are most easily decomposed by hydrofluoric acid. But those silicates not decomposable by the common acids (hydrochloric acid) show considerable difference in their comportment with hydrofluoric acid. The amorphous silicates, for instance all sorts of glass, in the form of a rough powder are easily decomposed; several of the crystalline silicates, for instance the felspars, must be reduced to an impalpable powder and allowed to stand a long time in contact with the acid, or to be submitted to heat; finally several, such as zircon and tourmaline, can be decomposed under the same conditions only with difficulty. The more easily a silicate can be decomposed and the more concentrated the acid, the more violent will be the action, that is, the elevation of the temperature of the mixture, which may even cause the fluid to boil.

It is not advisable to use a very concentrated, that is, a highly fuming hydrofluoric acid; the decomposition frequent-

ly takes place more easily when the acid is more dilute, besides there is this consideration, when the acid is fuming, it is exceedingly injurious to the health.

According to the authority of A. Mitscherlich, the decomposition of a silicate is effected more easily when it is heated with a mixture of hydrofluoric acid and two parts of dilute hydrochloric acid almost to boiling, which frequently produces a perfect solution. With those silicates which are more difficult of decomposition the fluid must be kept boiling for some time, taking care to renew the acid as it volatilizes.

If hydrofluoric acid is ready at hand, the object in view is most quickly attained. But the acid must be pure, that is, free from all non-volatile substances (lead, lime, alkalies).

The presence of silicic acid, more properly of hydrofluosilicic acid, is not injurious. If the acid has to be prepared, either fluor spar or kryolite is decomposed by means of concentrated sulphuric acid; the latter of these is to be preferred on account of its purity. The distillation is performed in a strong cylindrical vessel of lead with a loose-fitting lid which has to be luted with gypsum; to this lid is attached a platinum-tube growing wider and wider to conduct the vapors into a platinum dish containing water, into which the end dips through about two-thirds of this fluid. The platinum dish is covered with a concave piece of platinum foil, and placed in a vessel filled with quite cold water. The acid is caused to be evolved and passed through the water in the dish until this water has become sufficiently saturated with it.

The manner of submitting a silicate to the action of hydrofluoric acid is two-fold. Either the fine powder, previously weighed, is shaken into the prepared acid, or it is placed in the platinum dish, covered with water, and then the vapors of the acid are conducted upon it through the platinum tube to saturation. The latter method in general is to be preferred. Whichever way, however, be followed, it is always advisable afterwards to place the mixture aside for at least twelve hours.

In order to volatilize the fluoride of silicon and to convert the fluorides into sulphates, the fluid must be evaporated to dryness with sulphuric acid. The evaporation is effected on the water-bath, and as regards the success of the operation, it appears to be indifferent whether the sulphuric acid (not quite concentrated) is added at the beginning or after the evaporation to dryness. In every case the dish is kept over the water-bath as long as acid vapors are evolved, when these cease, it is placed over the flame of a lamp and heated to a higher temperature in order to drive off all excess of sulphuric acid; finally the temperature is raised until the bottom of the dish is of a low red heat. As soon as the dish has cooled, hydrochloric acid is poured upon the mass, which is digested for some time; after which a large quantity of water is added and the mixture is heated to boiling. It is now that we can judge, whether the silicate has been completely decomposed or not; if completely, the solution must be clear. It is only with silicates rich in lime, that the largest part of the sulphate of lime remains undissolved. But it happens not unfrequently, that there is a small quantity of residue, this is removed by filtration, it consists either of undecomposed substance or sulphate of baryta (strontia, lime) or titanitic acid, and requires, therefore, to be accurately investigated.

The acid solution of the bases is then examined for their determination according to the rules already given.

H. Rose recommends, instead of hydrofluoric acid, the employment of the acid fluoride of ammonium ($\text{HFl} + \text{AmFl}$), which naturally must be quite free from all impurities fixed in the fire. One part of the finely pulverized silicate is mixed in a platinum dish or in a capacious crucible with seven parts of fluoride of ammonium; water is then added and the mixture is stirred up into a pulpy consistence and cautiously heated until the mass is dry. The temperature is then raised to dark-red ignition and maintained at this heat as long as any vapors are evolved. Sulphuric acid is poured upon the residue, which is heated in order to drive off all excess

of sulphuric acid. The further treatment, digestion with hydrochloric acid, &c., has been given already. If there should remain any residue of undecomposed substance after solution, it must be heated again with fluoride of ammonium.

The separation of the bases is performed in general as with the silicates decomposable in acids, with the exception that the presence of magnesia modifies the course. It must, however, never be forgotten, that thereby no material, fixed in the fire, must be introduced into the analysis, and consequently the reagents must be quite free from such.

1. SILICATES containing NO MAGNESIA.

If the bases are alumina, lime, soda and potassa, the process is that on page 152. If to these are added protoxide of iron (protoxide of manganese), the processes on page 152 and 156 are combined.

2. SILICATES containing MAGNESIA.

BASES : alumina, lime, magnesia, soda and potassa. As soon as the alumina has been precipitated by ammonia, the lime by oxalic acid, the filtrate evaporated to dryness and the mass freed by heating in the crucible from the ammoniacal salt, the separation of the magnesia may be effected in two different ways:

a.)—The residue, consisting of the sulphates of magnesia and of the alkalies, is dissolved in the smallest quantity of water, to which is added a sufficient quantity of the concentrated solution of carbonate of ammonia (each litre containing 230 grammes of solid carbonate of ammonia and 180 grammes of ammonia of the specific gravity of 0.92). The mixture is well stirred together and then set aside for twenty-four hours. By this means the magnesia is precipitated completely as double carbonate of ammonia and magnesia. The precipitate is removed by filtration, washed with a quantity of the cold precipitant, dried, ignited and weighed as pure magnesia. The filtrate is evaporated to dryness; and the

residue is placed in a weighed porcelain crucible and heated cautiously and repeatedly with chloride of ammonium (vide page 161) in order to convert the sulphates into a mixture of chloride of potassium and chloride of sodium. This is weighed, dissolved and treated with chloride of platinum, &c., to effect the separation of potassa and soda (vide page 154).

OBSERVATION.—The precipitate of the double carbonate of ammonia and magnesia contains a small quantity of the corresponding alkaline salt, if this alkali happens to preponderate. After ignition the magnesia is then mixed with a little alkaline carbonate, which is extracted by means of hot water, after which the magnesia is weighed; and the alkaline extract is added to the filtrate.

b.)—The residue is dissolved in a large quantity of water; to the solution is added crystallized hydrate of baryta or a recently prepared solution of this substance; the solution is boiled for a few minutes and then filtered; finally the residue on the filter is washed with hot water, it consists of sulphate of baryta, magnesia and carbonate of baryta, whilst the filtrate, containing in addition to the alkalies an excess of baryta, becomes covered even during filtration with a film of carbonate of baryta.

The filter is digested with dilute hydrochloric acid, to this immediately a sufficient quantity of sulphuric acid is added so as to precipitate the baryta that has been dissolved, and then filtered. Ammonia is added in excess to the filtrate, and the magnesia is precipitated with phosphate of soda (vide page 133).

The filtrate containing the alkalies is digested with a mixture of ammonia and carbonate of ammonia; the carbonate of baryta is separated by filtration; the filtrate is evaporated to dryness; finally it is placed in a platinum crucible, to which hydrochloric acid is added in slight excess, and then the mixture is evaporated to dryness. The alkaline chlorides are ignited in a covered crucible at a low red heat, then they are weighed, and finally separated by chloride of platinum.

If the oxides of iron (manganese) are also among the bases, the course of the analysis is changed only in the manner already given.

D.—*Decomposition of Silicates by means of Sulphuric acid.*

Some silicates, upon which hydrochloric acid has scarcely any action at all, for instance magnesian mica, are completely decomposed by sulphuric acid. The substance is reduced either to an impalpable powder or in general to a fine state of division, then covered with a mixture of equal parts of concentrated sulphuric acid and water in a capacious platinum crucible, which is then covered and heated to boiling and maintained at this temperature until the mass is dry, after which it is raised gradually to a low red heat. As soon as it is cool, it is again moistened with sulphuric acid, and the evaporation and ignition are repeated. After these operations it is covered with a little hydrochloric acid, and digested; water is added; the mixture is heated; and the silicic acid is removed by filtration, and has afterwards to be tested as to its purity. The bases are separated according to the known methods, only bearing in memory, that they are partly in combination with sulphuric acid.

If this is employed to silicates rich in lime, it is possible that a part of the sulphate of lime separates at the same time with the silicic acid, which is afterwards converted by boiling with a solution of carbonate of soda into carbonate of lime.

According to A. Mitscherlich, such silicates as do not admit of being decomposed at all or imperfectly by this method, may be dissolved by heating a mixture of one part of the substance in question with two parts of water, and six parts of sulphuric acid in a glass tube hermetically sealed in an air-bath whose temperature ranges between 392°F. and 464°F. The possibility of an explosion requires, however, a special apparatus for this experiment.

Several silicates are not easily dissolved after fusion with bisulphate of potassa; and the separated silicic acid can not be obtained pure by washing.

E.—*Determination of the Degree of Oxidation of Iron in Undecomposable Silicates.*

It is an easy matter in silicates, that can be decomposed by acids, to show the presence either of the protoxide of iron or of the sesquioxide of iron or of both together, and to determine the amount quantitatively (vide page 152); but it is just the reverse in silicates that can not be decomposed by acids.

I. METHOD.—The fine powder is mixed in a platinum crucible with six times its weight of powdered calcined borax; a layer of this is then laid over the top of the mixture; the platinum crucible is placed in a larger crucible and embedded in magnesia; both are then covered and heated either in a gas-furnace (in which case a Hessian crucible will be a sufficient protection for the platinum crucible) to as intense a heat as possible and until the silicate has been fused in the borax (from a quarter to half an hour). The inner crucible together with its contents, is then weighed; after which the fused mass is loosened from the crucible by bending and pressure upon the sides, it is then reduced to a rough powder, weighed portions of which are used for repeating the experiment. The substance is dissolved in dilute hydrochloric acid, taking care to exclude all access of air, after which the amount of protoxide of iron is determined by the volumetric process with a solution of permanganate of potassa (vide page 65).

This method gives too small a quantity of iron, owing probably to the oxidation during the fusion with borax. If therefore the amount of protoxide of iron found by the volumetric iron test, be compared with the amount of iron found by means of the analysis and computed from the sesquioxide, there turns out to be a small amount of sesquioxide of iron even in those cases where the latter does not exist.

II. METHOD.—According to A. Mitscherlich the silicate in fine powder obtained by elutriation is exposed in an accu-

rately covered platinum dish with a mixture of hydrochloric and hydrofluoric acids to a temperature of nearly 212°F , until all is either dissolved or decomposed, after which the fluid is highly diluted with water, and submitted to the volumetric test for the protoxide of iron.

III. METHOD.—According to the same authority the silicate, reduced to a fine powder by elutriation, is decomposed in the way described on page 181 in a glass tube hermetically sealed, by means of sulphuric acid, after which the fluid is submitted to the volumetric iron test as before. If any sesquioxide of iron is present, it is reduced by zinc in a second experiment (vide page 64); and in this way the total amount of iron is determined.

F.—*Analysis of Mixed Silicates.*

Several stones in a crystalline condition consist of such silicates, of which one can easily be decomposed by acids, the other with difficulty, if at all. Since it is very important for our knowledge of stones to know intimately the minerals of which they are composed, and since no certainty in this respect can be drawn from an observation of them in their varied finely granulated forms, an analysis is of inestimable value in determining the nature of their constituents. Meteorites also (meteoric stones) are constituted in a great measure like the mixed rocky formations; and with these too the analysis under favorable conditions leads to a knowledge of their constituents. The principle of the analysis of such a mixture is to decompose one silicate by treatment with an acid, and then to determine the bases in combination with it, and which are now in the acid fluid. The residue, consisting of the silicic acid separated from the silicate, as well as of the whole amount of indecomposable silicate, is boiled with a solution of carbonate of soda in order to separate this silicic acid (whose amount is found either directly out of its solution or indirectly); after which the indecomposable silicate is analyzed by itself.

According to the nature of the silicate such a chemical operation can never be quite accurate, on account of its decomposability by acids, a circumstance alluded to (*vide* page 141), possessing properly speaking no sharp line of demarcation, but being merely one of degree, so that, the more concentrated the acid employed, the longer the time of its action, and the higher the temperature, so much the more of the so-called undecomposable silicate will undergo decomposition at the same time with the decomposable part. The result will be the more distinct and definite, the more opposite the two silicates are with regard to each other in their respective decomposabilities; for in this case a highly concentrated acid will not be employed. This is, for instance, the case, if the mixture consists of a silicate that gelatinizes with acids (nepheline, hauyne, olivine rich in iron, even anorthite) as is shown by my analyses of a pseudomorphous* specimen of leucite consisting of nepheline and vitreous felspar, and of the meteoric stones consisting of anorthite and augite by Juvenas and Stannern.†

Unfortunately, however, this favorable circumstance is relatively rare. If the decomposable silicate requires a concentrated acid (olivine containing but little iron), the other (augite, labrador) will be considerably attacked, and the result loses in definite character.

A further difficulty lies in the presence of other minerals in addition, which are met with sometimes either in minute quantities (accessory admixtures) or in larger quantities (as essential admixtures). If they are not silicates, but compounds soluble in acids, such as magnetic iron ore, titaniferous iron, sulphuret of iron or metallic iron (in meteorites combined with nickel, &c.), apatite, titanite, they may be sometimes removed by the magnet from the powdered material, or, in case their recognition is in any way possible, their amount may be computed from the quantity of one of the constituents peculiar to them as found by means of the

*Poggend. Ann. 98, 53.

†Poggend. Ann. 83, 585.

analysis. Pyrites or magnetic pyrites in this way is computed from the amount of sulphur, apatite from the phosphoric acid, titanite from the titanlic acid, and magnetic iron from the sesquioxide of iron. But it will easily be comprehended, that these expedients can not always be employed.

But it is quite impossible to make a sure computation of the analysis, if there are more than two silicates in the mixture, so that either the decomposable or the undecomposable part, or indeed both of them consist of several silicates. Thus for instance in several phonolites the undecomposable part, it is true, consists only of vitreous felspar, whilst the decomposable part is a mixture; in the lavas of Vesuvius the former is only augite, the latter, however, consists of a mixture of leucite, nepheline and other minerals; in several meteoric stones the earthy matrix as regards the decomposable part is only olivine, but the undecomposable part consists probably of several silicates; finally in basalt both parts are of a mixed nature. The computation of the analysis on the presupposed determined minerals therein is merely hypothesis; it indicates sometimes with equal probability two quite different minerals, and oftentimes the result is any thing but satisfactory.

These operations have especial reference to the analysis of mixed silicates, which do not admit of being separated by an acid, and which are analyzed as a whole, and then the attempt is made by computation to derive a solution as to their probable mixed constituents. Sometimes this can be done and with success, for instance if only two silicates are present, if their bases are not exactly the same, and the condition of the whole renders the presence of either one or the other of the constituents very probable. Suppose for instance we have a stone, which is either dolorite or a doloritic lava, and we analyze the whole, it will be easy enough to compute the relative quantities of labrodorite and augite, taking it for granted that augite is free from alumina, and that labrodorite contains no iron, which strictly speaking is not correct,

still the computation will not be essentially modified. Ascribing so much lime to the alkalies found as to give an amount of oxygen equal to one-third of that of the alumina, and so much silicic acid as to represent an amount of oxygen double that of the alumina, we thus get the amount of labrodorite; and the rest must be so constituted, if it is to be augite, that the oxygen of the protoxide of iron, of the magnesia and of the remaining lime must be half as much as that of the remaining silicic acid.

If it should happen in these mixed silicates that either of the constituents should present itself in large and separate particles, it would naturally be of essential service in leading to the denomination of the compound, and especially so if these separate particles can be analyzed alone.

The accurate analysis of compound silicates, among which may be reckoned also the meteorites, is indisputably a difficult task, in which we must be careful not to overlook several rare substances (oxides of chrominm and titanium).

BASALT.

We will take basalt as an example of a mixture of decomposable and uudecomposable silicates, and will suppose, that the modification to be analyzed, as is frequently the case, shows distinct particles of olivine and augite, and that the qualitative analysis has indicated the presence of carbonic acid, water and phosphoric acid together with small quantities of chlorine. Furthermore we will presuppose, that the magnet has extracted from the powdered stone black particles that turn out to be magnetic iron ore free from titanium.

A larger quantity of the stone, as much as will be necessary for the various experiments to be undertaken, is reduced to a fine powder, which is intimately mixed together and preserved in a close vessel.

a.)—One part is dried in the desiccator, as long as its weight undergoes any diminution. This gives the amount of the hygrometric water. The dried powder is ignited in

a crucible whilst dried carbonic acid is conducted through a hole in the cover to the contents, in order to prevent the oxidation of the protoxide of iron (of the magnetic iron, olivine and augite). The loss of weight gives the amount of water chemically combined. If the basalt should contain carbonic acid, that is, carbonate of lime, a part of it may escape, and this part may not be restored whilst cooling in a current of this gas. In this case we estimate the amount of carbonic acid in the ignited powder and compare it with the quantity obtained in *b*.

OBSERVATION.—When carbonate of the protoxide of iron is present the determination of the amount of water is not quite accurate, because this salt when ignited leaves behind ferroso-ferric oxide, and evolves carbonic oxide together with carbonic acid.

b.)—A part is decomposed in the carbonic acid apparatus (vide page 129) by means of hydrochloric acid; this gives the amount of carbonic acid.

c.)—A larger quantity (from six to nine grammes) is mixed intimately in a deep dish with a little water, then covered with a sufficient quantity of moderately concentrated hydrochloric acid, and the whole is heated, stirring the mixture all the while, until it becomes gelatinous. (In this experiment it is well either to weigh or measure the amounts of water and of acid, in order, in case the experiment should have to be repeated or for the volumetric analysis of iron, to be able to use the same proportion of substance for both experiments.) The mass is then diluted with water and filtered, and the gelatinous residue is washed with hot water. We have now: *A.*—The acid solution of the bases of the decomposable silicates and of the carbonates, together with the solution of magnetic iron ore and of apatite; *B.*—The silicic acid of the former together with the undecomposable silicates.

A.—This solution contains a certain amount of silicic acid; it has therefore to be evaporated to dryness, according to page 127, on the water-bath, &c. After the separation of the silicic acid a current of hydrosulphuric acid is passed through it, by which means small quantities of copper, tin, &c., are frequently indicated. As soon as the gas in excess has been dri-

ven off by heat, and the iron that has been reduced to the state of protoxide has again been oxidized by means of hydrochloric acid, ammonia is added in excess, and the bulky precipitate is removed by filtration and washed with hot water. It consists of sesquioxide of iron and of alumina, but it contains also a part of the magnesia, and also of the lime, besides protoxide of manganese and all the phosphoric acid. The lime exists, partly at least, as carbonate of lime, which has been formed during the filtration.

As soon as the precipitate has been dried, ignited and weighed, it is triturated, heated and weighed once more (because there has been incurred a trifling loss) and mixed with about as much pure silicic acid and six times its amount of carbonate of soda. The determination of the relative amounts of sesquioxide of iron and alumina is effected either as there indicated, or by fusion with hydrate of potassa (vide page 156). If the amount of manganese is so great as to render a separate determination apparently preferable, the process to be followed is found on page 179.

The filtrate from the precipitate by ammonia contains lime, magnesia and both the alkalis. It is analyzed as indicated on page 179. *B.*—In the next place the free silicic acid, which belongs to *A.* in the residue is separated from the undecomposable silicates; to effect this separation there is the choice of two methods.

Either the contents of the filter while still moist are transferred gradually into a boiling moderately concentrated solution of carbonate of soda, to which also at the last the filter is added; the mixture is then treated according to instructions on page 150. The residue is washed with hot water (if the filtrate is turbid, it is collected by itself, and as soon as it has settled, it is again filtered on a separate filter), dried, ignited* and weighed. It now represents the undecomposable silicates of the basalt. The alkaline solution is cautiously acidified with hydrochloric acid, warmed for some time and

*There is a slight inaccuracy produced here from the fact that the protoxide of iron of the augite is raised to a higher state of oxidation.

evaporated to dryness on the water-bath; the mass is now raised to a higher temperature, and all that is soluble is then extracted with water, and the separated silicic acid is collected on a filter. The weight of this is added to that which was received in *A*.

Or the residue is dried, ignited and weighed, and then transferred according to instructions given on page 150, into a boiling solution of carbonate of soda. The amount of the insoluble portion alone being determined from the weight, the difference will be the amount of the free silicic acid.

OBSERVATION.—The second method is by far the shorter of the two, but it has this disadvantage: the silicic acid after ignition is no longer as easily soluble as before. After boiling and diluting, therefore, the fluid is allowed to settle, the clear liquid is placed on the filter, and the residue is again boiled with carbonate of soda and water, &c. But even after repeated boiling such a residue always loses a little in weight, when the operation is undertaken afresh; this must not be forgotten in the computation.

The undecomposable silicates contain as bases, alumina, the oxides of iron and manganese, lime, magnesia, soda and potassa. Their amount must be large enough for two analyses to be made with them. One part is for the determination of the bases, with the exception of the alkalies; it is fused with carbonate of soda and treated according to instructions found on page 155, for the separation of the bases. The residue is decomposed with hydrofluoric acid, and the bases are determined (*vide* page 179) as regards iron and manganese.

d.)—One part is decomposed in a flask, taking care to exclude the air, and to pay attention to the observations in *c.* in reference to the quantities; a large quantity is then added, and then the mixture is submitted to the volumetric test with permanganate of potassa; by this means the amount of protoxide of iron in *A*. is obtained.

e.)—One part is decomposed at the ordinary temperature with nitric acid, spec. grav. 1.2; the mixture is then diluted and filtered; after which the chlorine, derived from the apatite, is precipitated with nitrate of silver. (The fluorine in the apatite does not admit of being determined directly, it can merely be computed by assuming the phosphoric acid and

the chlorine in the formula for apatite as a base.

X. ALUMINA and ALUMINATES.

Corundum and the compounds of alumina with strong bases (aluminates) are not acted upon by acid. They form a part of the spinel group, to which belong spinel, pleonaste (ceylonite, gahnite and chrome iron ore; whilst another part, in which the oxide of iron is substituted for alumina, (magnetic iron ore, magnoferrite, franklinite) is soluble in acids. The first mentioned are for the most part isomorphous mixtures, whose strong bases are magnesia, oxide of zinc, protoxide of iron, protoxide of manganese (perhaps also protoxide of chromium, whilst alumina is represented partly by the oxide of iron and of chromium, perhaps also the oxide of manganese) as a substitute.

These minerals, especially corundum, are so hard as to attack agate-mortars, and to become impregnated with silicic acid when pulverized therein. Steel mortars are, therefore, used for this purpose; and the powder is sifted through gauze; and the iron particles obtained by trituration are removed by hydrochloric acid.

The best method of dissolving corundum and the aluminates consists in fusing them with bisulphate of potassa. We are indebted to H. Rose for this plan. For the solution of chrome iron ore it is alone less adapted. A mixture is made in a capacious platinum crucible of one part of the substance in fine powder and four parts of sulphate of potassa also in powder, to this is added a sufficient quantity of concentrated sulphuric acid so as to produce a sort of thick gruel when stirred together with a stout platinum wire; the crucible is covered, with the exception of a small opening in the lid to allow the contents to be observed, and then cautiously heated, especially at the beginning, because it frequently happens that the contents are apt to foam over. Afterwards the heat is raised, and the mass is ignited, the crucible being now completely

covered up, and the ignition is kept up until the contents cease to give out any bubbles, and flow smoothly. Since the solvent action of the bisulphate of potassa depends solely on that part of the acid which converts the sulphate into the bisulphate, and since this part is volatilized by ignition, though slowly, and furthermore since the sulphate of alumina in like manner loses its acid under the same circumstances, it is frequently advantageous to moisten the cooled mass with sulphuric acid and to repeat the operations of heating and ignition for a short time.

The mass contains the bases as sulphates, it is digested when cold for some time with hydrochloric acid and afterwards mixed with a sufficient quantity of water and boiled. By this means all is dissolved, unless a portion should happen not to have been decomposed. In this case the undecomposed substance is removed by filtration and deducted.

The separate constituents are precipitated from the solution in the ordinary way.

According to A. Mitscherlich both corundum and the aluminates may be dissolved in sulphuric acid by exposing a mixture consisting of one part of the elutriated mineral, two parts of water and six parts of concentrated acid, hermetically sealed in a glass tube, to a temperature of about 410° F. for several hours.

1. ALUMINATE of MAGNESIA and PROTOXIDE of IRON.

(PROTOXIDE of MANGANESE.)

I. METHOD.—The acid solution of the fused mass is decomposed by means of chloride of ammonium in quantity proportionate to that of the magnesia. Ammonia is added in slight excess; and the mixture is then boiled until the vapors of ammonia have passed off. The magnesia is precipitated from the filtrate by means of ammonia and phosphate of soda. The precipitate is dried, ignited and weighed. It consists of oxide of iron (a trace of oxide of manganese) and

of alumina. In order to determine both of these, a portion is triturated to an impalpable powder, weighed and dissolved in a flask in hydrochloric acid; zinc at the same time being added to effect the reduction of the oxide of iron, after which the protoxide of iron is determined by the volumetric test with permanganate of potassa. (The precipitate, too, may be fused with hydrate of potassa according to the instructions given on page 156.)

II. METHOD.—Ammonia is added in slight excess to the solution, after which it is filtered, and the residue is washed with hot water. The magnesia is determined in the filtrate. The precipitate, which also contains magnesia, is fused, after it has been ignited and weighed, with hydrate of potassa (vide page 156); the alumina is either determined by the difference of weight, or precipitated from the alkaline solution according to the method found on page 156. The portion, that is insoluble in potassa, is dissolved in hydrochloric acid; the solution is then highly diluted and boiled (vide page 134) with carbonate and acetate of soda; and in this way the oxide of iron is separated from the magnesia.

If the quantity of manganese is more considerable, the methods found on pages 135 and 157 are employed.

2. CHROME IRON ORE.

(Vide the following article).

XI. COMPOUNDS of CHROMIUM.

Among the compounds of chromium we may mention *chromate of potassa*, *chromate of the oxide of lead* and *chrome iron ore* as particularly of importance; on this account we give the methods of their analysis here.

1. CHROMATE of POTASSA.

A weighed quantity of the salt is dissolved in a capacious flask in a small quantity of water, to this a proper amount of hydrochloric acid and double the quantity of alcohol are

added; the mixture is then boiled until the fluid appears of an intense green color. The chromic acid is by this operation reduced to the oxide of chromium, which remains in solution as chloride, together with chloride of potassium; whilst chloride of æthyle escapes. The fluid is placed in a dish; water is added, and heat is applied until the alcohol has all passed off. The oxide of chromium is then precipitated by neutralization with ammonia and afterwards sulphide of ammonium. The grey-green precipitate of the hydrated oxide of chromium is separated by filtration, washed, dried and ignited. It is then pure oxide of chromium, from whose weight the amount of chromic acid may be computed. The fluid is evaporated to dryness; the residue is placed in a platinum crucible and heated until the chloride of ammonium has been volatilized; the residual chloride of potassium is then ignited, keeping the crucible completely covered and avoiding too intense a heat. After it has been weighed, it is dissolved in water, and a small quantity of oxide of chromium, which sometimes occurs, is separated by filtration; this is weighed and added to the quantity previously obtained, but deducted from the weight of the chloride of potassium. From the latter we obtain the quantity of potassa in the salt.

OBSERVATION.—The commercial neutral chromate of potassa often contains no inconsiderable amount of sulphate of potassa. In this case the mass, remaining after the chloride of ammonium has been volatilized, is to be decomposed with sulphuric acid, again evaporated to dryness, intensely ignited and afterwards neutralized by means of carbonate of ammonia (vide page 113).

Although the amount of sulphuric acid may be computed, if the amount of the chromic acid and of the potassa is known, it may also be determined directly, with the reservation, however, not after the reduction of the chromic acid by the method above given, because of the easy formation of sulphuric ether, which can not be precipitated by any known base. On this account a fresh quantity of the salt is dissolved in a flask with water, to which hydrochloric acid is then added, it is then boiled for some time, by which a large proportion of the chromic acid is reduced and chrome is evolved. The fluid is then diluted with water, and the sulphuric acid is precipitated by chloride of barium; the precipitated sulphate of baryta is then washed on the filter with boiling water. If, after ignition, the residue should have a yellowish tinge (containing a little chromate of baryta), it is digested with a small quantity of hydrochloric acid and alcohol, after which it is again washed, dried, ignited and weighed.

2. CHROMATE of the OXIDE of LEAD.

(RED LEAD ORE, CHROME YELLOW, CHROME ORANGE,
CHROME RED, COLOGNE YELLOW.)

The substance, previously reduced to fine powder, is digested in a flask with hydrochloric acid and alcohol, until the fluid has assumed an intense green color, whilst the residue is a pure white. The former contains chloride of chromium; the latter is chloride of lead. This is collected on a filter (previously dried at a temperature of 248°F . and weighed), well washed with alcohol, and dried in the air and afterwards in the drying chamber, until it no longer loses any weight. From this dry chloride the quantity of oxide of lead is computed.

The alcoholic fluid is evaporated, after it has been mixed with water, until all vapors of alcohol have passed off; ammonia and sulphide of ammonium are then added, as in the preceding example, which precipitate the hydrated oxide of chromium; a small quantity of oxide remains in solution, which is obtained by evaporating the filtrate, ignition of the residue and treatment with water.

OBSERVATION.—Commercial chrome yellow frequently contains other substances, (and this is the case also with white lead) with which it is adulterated, partly in order to make it cheaper, and partly in order to modify its color. To this class of substances belong sulphate of baryta, sulphate of lime, sulphate of the oxide of lead, alumina, &c. These substances remain as a deposit with the chloride of lead, although it is difficult to determine their amount with complete accuracy, since, for example, the sulphate of lead is also partly converted into chloride of lead. The latter is boiled with water, as long as any thing dissolves; after which the amount of the residue is determined. Sulphate of baryta may in this way be determined with accuracy.

3. CHROME IRON ORE.

Chrome iron ore consists of the oxides of iron and chrome as constant constituents, and of alumina and magnesia as sometimes failing. It is not remarkably acted upon either by acids or by the alkaline carbonates as fluxes. If it is ignited with a mixture of carbonate of potassa and hydrated potassa, or with the carbonate and nitrate of an alkali (in a silver crucible), there is certainly a decomposition, oxide of chromium being converted into chromic acid, and the iron into oxide of iron, so that water dissolves the former together with the alumina as compounds of potassa, whilst the oxide of iron and magnesia remain behind; but the decomposition, even when

the ore has been elutriated, is always only partial; and it is difficult to determine the undecomposed part, of which besides we can not know with certainty whether the constitution is the same as that which has been decomposed or not.

But, on the other hand, chrome iron ore may be fused with bisulphate of potassa according to the method given on page 190. But very little of this is soluble in water from the fact, that a double sulphate of chrome and potassa has been formed which is insoluble in acids. On this account the mass, when cold is covered in the crucible with a mixture of carbonate of soda and saltpetre; the mixture is fused into a fluid mass (this operation slightly attacks the crucible). When cold it is thoroughly extracted with boiling water, then filtered; and the residue is washed with hot water.

The alkaline solution contains all the chromic acid and a part of the alumina. A considerable quantity of chlorate of potassa is added, it is then acidified with hydrochloric acid and evaporated down until it becomes somewhat consistent, adding from time to time a little chlorate of potassa. It is then completely dissolved in water; and the alumina is precipitated by ammonia. The filtrate is boiled for some time with hydrochloric acid, is allowed to cool; alcohol is added, in order to complete the reduction; after this the alcohol is distilled off; and the oxide of chromium is precipitated by ammonia and sulphide of ammonium (vide page 193).

The residue consists of iron, alumina and magnesia, which are determined according to instructions on page 191.

According to the authority of A. Mitscherlich, chrome iron ore is soluble in sulphuric acid, if the mixture is exposed in an hermetically sealed tube to the temperature of 210°F . (vide page 191).

If chrome iron ore is ignited in a current of hydrogen gas, its weight is very little diminished as proved by Moberg's experiments as well as my own. According to Rivot, on the contrary, if the temperature is sufficiently high, all the iron is reduced to the reguline condition, which may then be dis-

solved by dilute nitric acid. This, however, requires confirmation; and a better method of analysis is highly desirable.

XII. COMPOUNDS of TITANIUM.

Since certain minerals containing titanium, such as titanite and titanite iron, occur in many stones, and small quantities of titanite acid especially are frequently found in several minerals (for instance in hornblende, aemite), it can not be said, that titanium is a rare metal.

In the analysis of undecomposable silicates by means of carbonate of soda, the titanite acid can be found partly in the silicic acid and partly in the ammoniacal residue (alumina and oxide of iron). If we have to deal with a silicate, containing an alkali, and this has been dissolved by hydrofluoric acid, the residue which remains when the sulphates are dissolved (vide page 178), may also contain titanite acid, as well as the precipitate by ammonia.

The titanite acid is formed and determined in such residues and precipitates by fusion with bisulphate of potassa and by boiling the solution, as will be described more in detail in the following article.

1. TITANIC IRON.

The constituents of titanite iron are titanite acid, the oxide of iron, manganese and magnesia. Sometimes besides these are found small quantities of chromium, tin and lead.

A. General Analysis.—The substance reduced to a fine powder is fused (vide page 190) with bisulphate of potassa. For one part of the powder from six to eight parts of sulphate of potassa and the necessary quantity of sulphuric acid are taken and maintained in fusion for some time; the treatment, too, with sulphuric acid is repeated. As soon as the mass is cold, the crucible, together with its contents, is placed in a dish over which is poured a considerable quantity of

water; the whole is then allowed to stand, stirring frequently, until all is dissolved. No heat must be applied, because this would cause a turbidity or a precipitation of titanous acid. If any thing remains undissolved, it is either undecomposed titanous acid or silicic acid in admixture, which is removed by filtration and deducted. The clear solution is decomposed with a solution of sulphurous acid or with the bisulphite of an alkali, in order to convert the oxide of iron into the protoxide, and boiled for some time (about an hour), replenishing the water lost by evaporation, and adding also from time to time a little sulphurous acid. The titanous acid, that has been precipitated, is collected on a filter and washed with hot water. The filtrate is again heated to boiling, in order to be certain by a continuation of the boiling that no more titanous acid is precipitated. The titanous acid is dried, ignited and weighed.

OBSERVATION.—Notwithstanding every precaution the titanous acid frequently contains a small quantity of oxide of iron. The acid can be separated from the oxide by allowing it to settle after precipitation by boiling, by decanting the clear fluid, by dissolving the residue (in a platinum dish) in sulphuric acid, and by evaporating the solution, until the largest part of the acid in excess has been expelled. When this is cold, a small quantity of water is added gradually so as to avoid raising the temperature too high, the solution is then highly diluted and sulphurous acid is added; the mixture is then boiled as before prescribed. The small quantity of iron then remains in solution.

Any sulphurous acid that may remain in the filtrate is driven off by heat, chlorate of potassa is then added in order to oxidize the iron, afterwards chloride of ammonium and ammonia are added in excess. In this way the oxide of iron (together with a little oxide of manganese) is precipitated. In the filtrate are estimated lime and magnesia. The oxide of iron may be also separated from the earths by means of carbonate of soda and acetate of soda (vide page 134). If the amount of manganese is considerable, and has to be determined, proceed as indicated on page 135.

B. Determination of the Degree of Oxidation of the Iron.

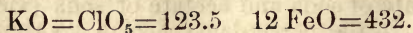
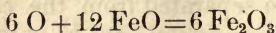
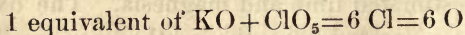
This is best effected by the volumetric process, for which there are two methods:

a.)—The substance reduced to the most impalpable powder possible is boiled in a vessel from which air is excluded

for some time with hydrochloric acid, until it is dissolved, that is, until the black color has disappeared. If there is much titanitic acid present, a small quantity separates. The solution is diluted, and is then poured into a large quantity of water in which the protoxide of iron is determined by permanganate of potassa in the volumetric process.

b.)—The titanitic acid is dissolved as before in hydrochloric acid. The solution, as soon as it is cold, is placed in the same flask which forms a part of the apparatus described on page 45, and is mixed with an accurately measured quantity of a dilute solution of chlorate of potassa, of a given strength as described on page 45.

A quantity of this solution is taken containing an amount of the chlorate sufficient to oxidize all the iron found in A., if present in the form of protoxide. The solution is placed in a pipette and is allowed to flow into the flask, at the same time the cork with the bent glass tube is quickly placed where it belongs, whilst the other end of the tube dips into the solution of iodide of potassium. By heating and boiling, the chlorine is driven out, which releases an equivalent quantity of iodine, which is determined by means of sulphurous acid and a standard solution of iodine. By this means we ascertain how much chlorate of potassa has not been used for the oxidation of the protoxide of iron. The difference gives the quantity used, and from this is derived the quantity of the protoxide of iron.



Therefore one part of chlorate of potassa converts 3.52653 parts of protoxide of iron into the sesquioxide.

XIII. COMPOUNDS of FLUORINE.

The mode of determining fluorine, when the metallic fluorides are in combination with the phosphates or silicates, has

already been shown on pages 191 and 170. At present we have to deal with their analysis, when they occur alone.

The most common fluorides are fluor spar (fluoride of calcium) and cryolite (the double fluoride of aluminum and sodium). We select the latter as an example.

1. CRYOLITE.

The substance in fine powder is heated in a platinum crucible with concentrated sulphuric acid, until the decomposition is complete and also the largest part of the acid in excess has been driven off. The mass when cold is digested with a small quantity of hydrochloric acid, and the sulphates of alumina and soda are dissolved in water. The first of these is precipitated by ammonia or sulphide of ammonium; the filtrate is evaporated to dryness; after which the residual sulphate of soda is ignited and rendered neutral by carbonate of ammonia (vide page 113).

The amount of fluorine is found by the loss.

XIV. STECHIOMETRICAL COMPUTATION OF THE ANALYSIS.

CONSTRUCTION of a FORMULA.

As soon as the analysis is completed, and the quantities of the constituents of the substance analyzed have been computed, by aid of the tables, from the amount of the precipitates, &c., found, it is customary for the sake of comparison to ascertain the percentage of each component of the substance investigated. This is the *empirical result*.

If all the constituents of a body have been determined without exception in a direct manner, it will invariably happen that either a *loss* or an *excess* will be the result. The former is inevitable and is to be attributed to the different manipulations, and increases with their number; on this account, as already remarked (vide page 3), every unnecessary manipu-

lation, for example, every unnecessary change of vessel must be carefully avoided. The loss, therefore, seems to stand in a certain ratio with the number of the constituents; nevertheless this must be taken only in a general sense, since the loss depends essentially on the nature of these constituents, from the fact that many bodies admit of being determined with greater accuracy than others.

If a substance contains only two or three constituents, the loss by the analysis at the highest ought not to amount to more than 0.5 per cent; whereas if the substance is a very complicated mixture or consists of constituents that can with difficulty be determined, the loss may amount to 2 per cent without the implication of any great error in the analysis.

In every case, in the summation of the result, the loss must be given with all honesty and uprightness; for the method of dividing it up among all the constituents in proportion to their respective quantities, in order to make it disappear, as is sometimes the practice, is to be avoided altogether. For it is easy to conceive, that the loss may be attributed in preference to either one or other of the constituents; and it is evident, that the one first separated in all probability will be more correct, than those determined afterwards.

An *excess* in analyses is either *real* or only *apparent*. The first occurs with beginners just as frequently as the contrary, a loss, and arises in general from the imperfect washing of the precipitates, a manipulation that has to be performed with great care. It is no rare occurrence to find that a precipitate, which is taken for a pure oxide, is in reality either a basic salt or a double salt, and that thus either the acid or the base is the cause of the excess in question. For instance, suppose that magnesia is precipitated by an alkaline carbonate, it may happen under certain circumstances, that a double carbonate will be thrown down; alumina, that has been precipitated from a solution containing potassa and sulphuric acid, easily retains a part of either base; and sulphate of baryta, thrown down from solutions containing nitric acid, al-

ways contains nitrate of baryta. All such circumstances, that are liable to give rise to error of the kind in question, require to be known; and, on this account frequent mention has been already made of them. In every case, in which the excess is to be attributed to this cause, the analysis has to be repeated.

An *apparent* excess always occurs in analyses, which in other respects are quite accurate, if a constituent exists in the compound either in the reguline condition or in the form of a lower oxide, which the direct result oxidizes or presents as a higher oxide; as for instance, in a compound containing iron in the form of protoxide, which is always determined as sesquioxide in the estimation of iron. Sometimes this excess may serve as the simplest proof of the presence of the protoxide, in those cases where (with silicates not decomposable by acids) it is difficult to arrive at any positive evidence, by means of a qualitative examination, of the presence of either the protoxide or the sesquioxide. In compounds containing fluorine an excess is sure to be produced, if the electro-positive constituents are altogether determined in the form of oxides. This is the case with the different forms of topaz: silicic acid, alumina and fluorine; and the best analyses indicate an excess varying between 6 and 8 per cent, arising from the oxygen of those quantities of silicic acid and alumina which existed in the compound as silicon and aluminium with fluorine.

It has already been observed (vide page 9) that, as soon as an analysis is complete, it becomes necessary to test the respective constituents obtained, as to their purity.

STOECHIOMETRICAL COMPUTATION of an ANALYSIS.

As it is only with purely chemical compounds, and not with mixtures, that such a computation is possible, it is evident that it can not be applied to every analysis. The analytical investigation of mixtures is indeed very important, although in general it is of value only for technical purposes,

as is the case with slags, glasses, alloys, &c; nevertheless such mixtures frequently approximate so nearly to purely chemical compounds, as to allow them to be submitted to a stoëchiometrical computation, and to deduce from their analysis a chemical formula, approximatively at least, corresponding to them.

The aim of the stoëchiometrical computation is to search for the relative and the absolute number of equivalents in which each constituent exists in the compound. Since now every chemical compound consists of a fixed number of constituents, that is, since it can contain its constituents only in accordance with the ratio of weights, which corresponds to one or several equivalents (atoms) of these constituents, it is evident that, when an analysis of a substance shows such a ratio of weights, the substance itself must be a chemical compound, and not a mixture.

The stoëchiometrical computation of an analysis shows whether the substance under investigation is a chemical compound or not. But supposing a substance has been analyzed, whose characters in other respects indicated beforehand such a compound (for example the crystalline condition), and for all that the result is found not to accord with the laws of definite proportions, that is, the weights of the constituents do not stand in the same ratio to each other as the chemical equivalents or atomic weights or their multiples do to each other; this is a proof that either the analysis is erroneous, or the substance is not pure (crystals may contain foreign ingredients enclosed in their substance). In such cases and for such reasons the computation exercises an important control as regards the accuracy of the analysis.

THE GENERAL MODE of making the COMPUTATION.

The analysis has already furnished us with the relative amounts of weight of the constituents, and the question now presents itself: What is the relative number of atoms (chemical equivalents) of these constituents?

Divide the weight of each constituent by the chemical equivalent (atomic weight) of this constituent. The quotient expresses the number of chemical equivalents or atoms.

Example.—The analysis of a specimen of zinc blende by Arfvedson gave the following:

Zinc	66.34
Sulphur	33.66
	<hr/> 100.00

The question is: How many equivalents of these elements constitute the combination?

The equivalent (atomic wt.) of zinc is 32.5, and that of sulphur is 16.

We have therefore

$$\frac{66.34}{32.5} = 2.041, \text{ and } \frac{33.66}{16.0} = 2.10$$

The quotients 2.04 and 2.10 or 204 and 210 express, therefore, the relative number of equivalents comprehended in the formation of zinc blende. These two numbers are in the ratio of 1 : 1.03 or of 0.97 : 1, that is, so near to the ratio of 1 : 1, that the difference may be attributed to some error in the analysis.

Such deviations from simple ratios occur in the computation of every analysis, and are the consequence of the errors attached to every empirical operation. It is on this account, that stoichiometrical computation aims to ascertain the right chemical proportions, and in accordance with these to apply afterwards the correction to the quotients found. The smaller the correction to be applied, the more correct will be the analysis. If a proportion is found lying between two simple ratios, it will remain doubtful, which is the right one. In such a case the analysis is of no use for the stoichiometrical computation; and the substance was either a mixture, or the numerical results of the analysis are not correct.

If the analysis of the zinc blende in the preceding example had shown, that zinc and sulphur exist in the compound atom for atom, or in the ratio of single equivalents, the *formu-*

la or symbol will be ZnS.

The most intelligible way of exhibiting the degree of accuracy of an analysis consists in placing the *computed* composition side by side with that which has been *found*. The former is obtained by the addition of the chemical equivalents of the formula and by the reduction of the sum to 100.

1 equivalent of zinc	= 32.5	= 67.01
1 „ „ sulphur	= 16.0	= 32.99
	<hr/> 48.5	<hr/> 100.00

$$48.5 : 32.5 :: 100 : x \quad x = 67.01$$

$$48.5 : 16.0 :: 100 : y \quad y = 32.99$$

If we now place the composition of the compound, as derived from the analysis, side by side with that computed, we have:

	Found:	Computed:
Zinc	66.34	67.01
Sulphur	33.66	32.99
	<hr/> 100.00	<hr/> 100.00

From this it will be observed, that there is either 0.67 zinc too little, or 0.67 sulphur too much.

OBSERVATION.—If, as in the preceding example, the analysis gives the exact sum of 100 parts, one of the two constituents was not determined by a direct method, but was simply deduced by subtraction of its weight from the 100 parts employed. This was the case with the sulphur. It may, therefore, be said, that the analysis has given 0.67 too much sulphur.

This is the mode of proceeding with the computation of every analysis. By means of the (*empirical*) formula the *computed* (*theoretic*) constitution of a compound is sought for, and this is then placed side by side with that which has been *found*.

Copper Pyrites.—H. Rose found in a crystallized specimen of this substance:

Sulphur	35.87	1 equivalent = 16
Copper	34.40	„ = 31.7
Iron	30.47	„ = 28
	<hr/> 100.00	

The division of the respective parts of 100 by their chemical equivalents gives:

$$\frac{35.87}{16} = 2.24 \quad \frac{34.40}{31.7} = 1.09 \quad \frac{30.47}{28} = 1.09.$$

The three quotients 2.24, 1.09 and 1.09 have the ratio of 2.05 : 1 : 1, or so near to 2 : 1 : 1, that this ratio is undoubtedly the true one; from this we see that copper pyrites consists of two atoms of sulphur, one atom of copper and one atom of iron, which is expressed by the empirical formula: $\text{Cu} + \text{Fe} + 2\text{S}$, or numerically:

$$\begin{array}{rcl} 2 \text{ equivalents of sulphur} & = & 32.0 \\ 1 \quad \quad \quad \text{copper} & = & 31.7 \\ 1 \quad \quad \quad \text{iron} & = & 28.0 \\ & & \hline & & 91.7 \end{array}$$

which, reduced to parts of 100, are as follows:

$$\begin{array}{rcl} 91.7 : 32.0 :: 100 : x & & x = 34.90 \\ 91.7 : 31.7 :: 100 : y & & y = 34.57 \\ 91.7 : 28.0 :: 100 : z & & z = 30.53 \end{array}$$

The composition, therefore, of copper pyrites is:

	Computed:	Found:	Differences:
Sulphur	34.90	35.87	+ 0.97
Copper	34.57	34.40	— 0.17
Iron	30.53	30.47	— 0.06
	<u>100.00</u>	<u>190.74</u>	

From the differences annexed it will be perceived, that too much sulphur and too little copper and iron have been found, and that the sulphur is the least accurate element in the compound. The difference of sulphur is almost six times as great as that of copper, or sixteen times as great as that of iron. Since

$$34.90 : 35.87 :: 100 : 102.8$$

$$34.57 : 34.40 :: 100 : 99.5$$

$$30.53 : 30.47 :: 100 : 99.8$$

we may say, that

$$\text{the excess of sulphur} = 2.8 \text{ per cent,}$$

$$\text{,, loss ,, copper} = 0.5 \text{ ,, ,,}$$

$$\text{,, ,, ,, iron} = 0.2 \text{ ,, ,,}$$

The excess of the sum of the substances found by the ana-

$\text{HIO} = 9$; we have therefore

$$\frac{32.13}{39.7} = 0.809; \frac{31.57}{40.0} = 0.789; \frac{36.30}{9.0} = 4.033$$

Dividing the quotients by the smallest, they have the ratio of 1.055 : 1 : 5.111, thus evidently = 1 : 1 : 5, that is, sulphate of copper is a compound of one equivalent of oxide of copper, one of sulphuric acid and five of water. The corresponding formula is $\text{CuSO}_3 + 5\text{Aq.}$, from which we derive by reduction :

1 equivalent of oxide of copper	39.7	=	31.84
1 ,, sulphuric acid	40.0	=	32.08
5 ,, water	45.0	=	36.08
	<u>124.7</u>		<u>100.00</u>

The differences are consequently

Oxide of copper	+	0.29
Sulphuric acid	—	0.51
Water	+	0.22

Silicate of the Oxide of Zinc.—In a specimen of this mineral were found :

Chem : Equiv : Quotients.

Silicic acid	25.30	30.0	$\frac{25.30}{30.0} = 0.845$
Oxide of zinc	67.74	40.5	$\frac{67.74}{40.5} = 1.672$
Water	7.54	9.0	$\frac{7.54}{9.0} = 0.838$

The three quotients are to each other as 1 : 2 : 1; the silicate of the oxide of zinc is consequently a compound of one equivalent of silicic acid, two equivalents of the oxide of zinc and one equivalent of water, corresponding to the formula $\text{Zn}_2\text{O}_2\text{SiO}_2 + \text{Aq.}$, which numerically gives :

1 equivalent of silicic acid	=	30	=	25.0
2 ,, oxide of zinc	=	81	=	67.5
1 ,, water	=	9	=	7.5
		<u>120</u>	=	<u>100</u>

Here the differences of the analysis are :

Silicic acid	+	0.30
Oxide of zinc	+	0.24
Water	+	0.04

Sodalite.—A specimen of sodalite from the Uralian mountains gave :

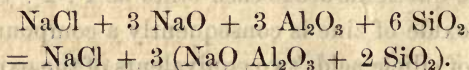
Chlorine	7.10
Silicic acid	38.40
Alumina	32.04
Soda	24.75
	<hr/> 102.29

The excess of 2.29 per cent is only apparent, since the chlorine is in combination with sodium in the compound, whilst the latter is computed as soda.

The chemical equivalents are: $\text{Cl} = 35.5$, $\text{SiO}_2 = 30$, $\text{Al}_2\text{O}_3 = 51.4$, $\text{NaO} = 31$; the quotients therefore are:

$$\frac{71.0}{35.5} = 0.2, \quad \frac{38.40}{30} = 1.28, \quad \frac{32.04}{51.5} = 0.624, \quad \frac{24.75}{31} = .8$$

These quotients, when divided by 0.2, have the ratio of 1 : 6.1 : 3.1 : 4, that is, of 1 : 6 : 3 : 4, so that sodalite is a compound of one equivalent of chlorine, six equivalents of silicic acid, three equivalents of alumina and four of soda. Since now one equivalent of chlorine requires one equivalent of sodium in order to produce one equivalent of chloride of sodium, sodalite contains, properly speaking, three equivalents of soda, or it consists of one equivalent of chloride of sodium and a silicate of alumina and soda, corresponding to the formula :



Numerically and reduced to the ratio of 100, this formula gives:

$$\begin{array}{lcl} 1 \text{ equivalent of chlorine} & = & 35.5 = 7.31 \\ 1 \text{ ,, sodium} & = & 23.0 = 4.73 \\ 6 \text{ ,, silicic acid} & = & 180.0 = 37.06 \\ 3 \text{ ,, alumina} & = & 154.2 = 31.75 \\ 3 \text{ ,, soda} & = & 94.0 = 19.15 \\ & & \hline & & 485.7 \quad 100.00 \end{array} \quad \left. \vphantom{\begin{array}{lcl} 1 \text{ equivalent of chlorine} \\ 1 \text{ ,, sodium} \\ 6 \text{ ,, silicic acid} \\ 3 \text{ ,, alumina} \\ 3 \text{ ,, soda} \end{array}} \right\} = \text{NaCl } 12.04$$

In order to be able, however, to make a direct comparison between the computation and the analysis, the 4.73 for sodi-

um must be converted into 6.38 for soda, which with the 19.15, already for soda, gives together 25.53 per cent for soda. The analysis therefore ought to have given:

Chlorine	7.31
Silicic acid	37.06
Alumina	31.75
Soda	25.53
	<hr/> 101.65

in which the excess, 1.65 per cent, corresponds to the oxygen required to convert sodium into soda.

The differences of the analysis are:

Chlorine	— 0.21
Silicic acid	+ 1.34
Alumina	+ 0.29
Soda	— 0.78

Ruby Silver.—Bonsdorff found in a specimen of dark ruby silver from Andreasburg:

		Equiv:	Quotients.
Sulphur	17.78	16	$\frac{17.78}{16} = 1.11$
Antimony	23.26	120.3	$\frac{23.26}{120.3} = 0.19$
Silver	58.96	108	$\frac{58.96}{108} = 0.55$
	<hr/> 100.00		

The three quotients have the ratio of 6.4 : 1 : 2.9, which = 6 : 1 : 3, from this it is seen that there are present 6 equivalents of sulphur, 1 equivalent of antimony and 3 equivalents of silver. This is expressed by the empirical formula $3 \text{ Ag} + \text{Sb} + 6 \text{ S}$, which numerically gives:

6 equivalents of sulphur	=	96	=	17.77
1 " antimony	=	120.3	=	22.26
3 " silver	=	324	=	59.97
		<hr/> 540.3		<hr/> 100.00

The differences are:

Sulphur	+ 0.01
Antimony	— 1.00
Silver	— 1.01

Computation of the Proportion of Oxygen (Sulphur) in the Acid and the Base.

The stoëchiometrical computation of the secondary combinations is obtained by first getting the relative weight of the common constituent in the two primary combinations, of which the secondary combination consists. This is known to be always definite and in general very simple.

This mode of computation is therefore applied firstly to the great class of oxygen salts, then to the sulphur salts and the haloid double salts. We will employ the examples already given, as far as they refer to this subject, in illustration of our remarks.

Sulphate of Copper.—Oxide of copper contains 20.14 per cent of its weight of oxygen, sulphuric acid $\frac{3}{8}$, and water $\frac{8}{9}$. We have therefore:

$$\begin{array}{rclcl} 100 : 20.14 :: 32.13 : x & & x = & 6.47 \\ 5 : 3 :: 31.57 : y & & y = & 18.94 \\ 9 : 8 :: 36.30 : z & & z = & 32.27 \end{array}$$

The numbers 6.47 : 18.94 : 32.27 are = 1 : 2.9 : 5. The next simple ratio is 1 : 3 : 5. Thus the acid in sulphate of copper contains three times as much oxygen, and water five times as much oxygen as the base, and since one equivalent of sulphuric acid contains 3 equivalents of oxygen, and one equivalent of water contains 1 equivalent of oxygen, it is evident the same result is obtained by this mode of computation as by the preceding, namely, that sulphate of copper consists of 1 equivalent of oxide of copper, 1 of sulphuric acid and 5 equivalents of water.

Calamine.—Since silicic acid contains 53.3 per cent of oxygen, and the oxide of zinc 19.75 per cent, we find that:

$$\begin{array}{rcl} 25.30 \text{ silicic acid} & = & 13.48 \text{ oxygen} \\ 67.74 \text{ oxide of zinc} & = & 13.38 \text{ „} \\ 7.54 \text{ water} & = & 6.70 \text{ „} \end{array}$$

The quantities of oxygen have the ratio to each other of 2 : 1.997 : 1, consequently as 2 : 2 : 1, which again leads to the formula $2 \text{ ZnO} + \text{SO}_2 + \text{Aq.}$

Sodalite.—The equivalents of chlorine and oxygen have the ratio to each other of $35.5 : 8 :: 4.4376 : 1$. alumina contains 46.8 per cent, and soda 25.8 per cent of oxygen. The quantities of oxygen therefore corresponding to

7.10 chlorine	=	1.60 oxygen
38.40 silicic acid	=	20.47 „
32.04 alumina	=	14.99 „
24.75 soda	=	6.38 „

The quantity of sodium in combination with chlorine corresponds to 1.6 of oxygen, and there remains 4.78 for that quantity of oxygen which goes to the formation of soda. The ratios $4.78 : 14.99 : 20.47 = 1 : 3.1 : 4.5$, which are nearly $= 1 : 3 : 4$, the silicate is $\text{NaO} + \text{Al}_2\text{O}_3 + 2 \text{SO}_2$, and since $1.60 : 4.78 :: 1 : 3$, we see that 1 equivalent of chloride of sodium is in combination with 3 equivalents of the silicate.

Observation.—Also here we see quite distinctly, that the analysis has given too much silicic acid, so much indeed as to raise the question whether the proportions of oxygen, instead of being as $1 : 3 : 4$, might not be as $1 : 3 : 4.5 = 1 : 6 : 9 = 4 : 12 : 18$, corresponding to the formula $4 \text{NaO} + 4 \text{Al}_2\text{O}_3 + 9 \text{SiO}_2$, if this were not in opposition to the results obtained by other analyses of sodalite.

With the sulphur salts this mode of computation is the more important inasmuch as the element common to both the acid and the base, namely sulphur, is determined directly, and the computed quantity will approximate the more nearly to that which is found, according as the analysis is more correct.

Ruby Silver.—If we assume, that antimony is represented by SbS_3 , and silver by AgS , and that the former contains 28.5, the latter 12.9 per cent of sulphur, we have:

$$\begin{array}{rcl} 71.5 : 28.5 :: 23.26 : x & x = & 9.27 \\ 87.1 : 12.9 :: 58.96 : y & y = & \frac{8.73}{18.00} \end{array}$$

The quantity of sulphur found was 17.78 per cent; if therefore the two metals had been estimated correctly, the quan-

tity found would be too little by only 0.22 per cent. The proportions of sulphur, required by antimony and silver, and in simple relation to each other, are as 1.06 : 1, evidently therefore as 1 : 1; and since 1 equivalent of sulphate of antimony contains 3 equivalents of sulphur, and 1 equivalent of sulphide of silver contains 1 equivalent of sulphur, it follows that the combination consists of 1 equivalent of sulphide of antimony and 3 equivalents of sulphide of silver, corresponding to the formula $3 \text{ Ag S} + \text{Sb S}_3$.

Cryolite.—The analysis by Berzelius of this substance, which consists of fluorine, aluminium and sodium, gave:

Sodium	32.93
Aluminium	13.00
Fluorine (loss)	54.07
	<hr/> 100.00

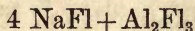
Assuming that the two fluorides correspond to the known oxides of the metals, the fluoride of sodium will consist of 1 eq: of sodium and 1 of fluorine, the fluoride of aluminium of 2 eq: of aluminium and 3 equivalents of fluorine. Since the eq: of Na=23, of Al=13.65 and of Fl=19 we have:

$$23.0 : 19 :: 32.93 : x \quad x = 27.20$$

$$27.3 : 57 :: 13.00 : y \quad y = 27.14$$

$$\hline 54.34$$

The quantities of fluorine are evidently equal, therefore cryolite consists of 3 equivalents of fluoride of sodium in combination with 1 equivalent of fluoride of aluminum, corresponding to



This formula numerically represented gives:

3 equivalents of sodium	= 69	= 32.81	= NaFl	59.91
2 „ aluminium	= 27.3	= 12.98	= Al_2Fl_3	49.99
6 „ fluorine	= 114.0	= 54.21	=	
	<hr/> 210.3	<hr/> 100.00		

Computation of isomorphous Mixtures.—An isomorphous mixture consists of two or several isomorphous compounds, which as a rule are analogously combined and in general hold

in common either one or the other more proximate constituent. The computation of its formula is two-fold: general and special.

The General Computation regards it as a single compound, in which one part of the one constituent is, as it were, substituted by an equivalent quantity of an isomorphous body. The respective numbers constituting 100 are divided by their corresponding chemical equivalents, the quotients of the isomorphous bodies are added together and, the sum is compared with the remaining quotients.

Smaltine.—A specimen of this substance analyzed by Riechelsdorf gave:

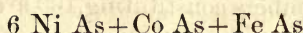
Chem: Equiv: Quotients.

Arsenic	72.64	75	$\frac{72.64}{75}$	0.969	
Nickel	20.74	29	$\frac{20.74}{29}$	0.715	} 0.943
Cobalt	3.37	39	$\frac{3.37}{39}$	0.112	
Iron	3.25	28	$\frac{3.25}{28}$	0.116	
	100.00				

If we denote the electro-positive metals nickel, cobalt and iron by R, the sum of their equivalents has a ratio to that of arsenic as 1 : 1.03, which is evidently = 1 : 1; the general formula for the mixture, RAs, tells us that each of the three isomorphous bodies contained in the mineral consists of one equivalent of the two constituents, that is, NiAs, CoAs and FeAs.

The Special Computation of an isomorphous mixture aims to determine the number of equivalents of the separate isomorphous compounds, in order to evolve from this the *special* formula. It consists in eliciting the ratio in which the separate quotients of the isomorphous bodies stand with regard to each other, a ratio which in truth is always definite, but not always as *simple* as that of the components in a real compound.

In the preceding example the equivalents of iron, cobalt and nickel have the ratio to each other of 116 : 112 : 715 : = 1 : 1 : 6.4. Let us assume the ratio to be 1 : 1 : 6, that is, one equivalent of iron, one of cobalt and six of nickel, or that the mixture consists of one equivalent of arsenide of iron, one of arsenide of cobalt and six of arsenide of nickel. In this case the special formula will be:

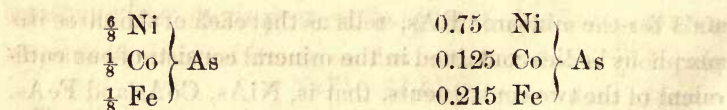


which numerically gives:

8	equivalents of arsenic	=	600	=	72.11
6	„ nickel	=	174	=	20.92
1	„ cobalt	=	30	=	3.60
1	„ iron	=	28	=	3.37
			<hr/> 832		<hr/> 100.00

In such a special computation we are frequently in the habit of representing the mixture as a single compound, for instance of the most predominant constituent, of reducing the formula and computation to 1 equivalent of the same, and of specifying the ratio in which the isomorphous constituents stand in regard to each other.

In the case just given, of the 8 equivalents 6 equivalents = $\frac{6}{8} = \frac{3}{4}$ nickel, $\frac{1}{8}$ cobalt and $\frac{1}{8}$ iron. The compound is therefore represented as arsenide of nickel, NiAs, in which $\frac{1}{8}$ of the nickel is displaced by cobalt, and $\frac{1}{8}$ by iron; the formula then stands:



and by computation and reduction we have;

1	equivalent of arsenic	=	75	=	72.11
$\frac{3}{4}$	„ nickel	=	21.75	=	20.92
$\frac{1}{8}$	„ cobalt	=	3.75	=	3.60
$\frac{1}{8}$	„ iron	=	3.5	=	3.37
			<hr/> 104.00		<hr/> 100.00

Naturally $104 = \frac{1}{8}$ of 832.

If the formulae of isomorphous mixtures are written in this

abbreviated way, the different symbols of the isomorphous constituents are regarded altogether as one equivalent (unless there should be a number behind them).

If in an isomorphous mixture one or more of the isomorphous bodies should exist in very minute quantities when compared with the principal component, these small quantities are converted, in the computation of the analysis, into an equivalent quantity of the principal constituent, and consequently the mixture itself into a compound of this constituent, and from this the equivalents of the two constituents are computed.

Since the equivalents of iron, nickel and cobalt are in the ratio of 28 : 29 : 30, we have:

$$\begin{array}{rcl} 30 : 29 :: 3.37 : x & x = 3.26 & \text{nickel.} \\ 28 : 29 :: 3.25 : y & y = \frac{3.37}{6.63} & \text{,,} \end{array}$$

The whole, regarded as pure arsenide of nickel, would therefore become :

		Quotients
Arsenic	72.64	$\frac{72.64}{75} = 0.969$
Nickel	27.37	$\frac{27.37}{29} = 0.944$

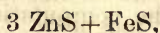
which, since each constituent is present as a single equivalent, will be represented by the formula NiAs; and, since 6.63 is nearly equal to $\frac{1}{4}$ of 27.37, $\frac{1}{4}$ of the nickel is displaced by cobalt and iron, whose quantities again are nearly equal to each other.

Zinc Blende.—A specimen of black zinc from South America gave :

Chem : Equiv :			Quotients.		
Sulphur	33.73	16	$\frac{33.73}{16} = 2.108$	}	2.11
Zinc	51.95	32.5	$\frac{51.95}{32.5} = 1.6$		
Iron	14.32	28	$\frac{14.32}{28} = 0.51$		

Since $2.108 : 2.11 :: 1 : 1$, the whole mixture = RS, R being regarded as = ZnFe.

Again since $9.51 : 1.6 ::$ nearly $1 : 3$, that is, there are present 1 equivalent of iron and three equivalents of zinc; the whole is an isomorphous mixture of 1 equivalent of sulphide of iron and 3 equivalents of sulphide of zinc.



which numerically gives:

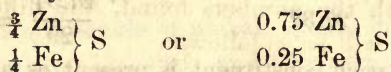
4 equivalents of sulphur	=	64	=	33.95
3 „ zinc	=	96.5	=	51.19
1 „ iron	=	28	=	14.86
		<u>188.5</u>		<u>100.00</u>

The same result will naturally be obtained by computing the quantity of sulphur required by each of the two metals in order to form RS. Thus

$$\begin{array}{rcl} 32.5 : 16 :: 51.95 : x & x = & 25.58 \text{ sulphur} \\ 28.0 : 16 :: 14.32 : y & y = & \frac{8.18}{33.76} \text{ „} \end{array}$$

The two amounts of sulphur have the ratio nearly of $3 : 1$.

From the preceding it follows, that the special formula of this zinc blende may be written:

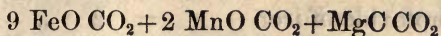


Chalybite.—In a specimen, a variety of this mineral, from Siegen were found:

	Chem : Equiv : Quotients.		
Carbonic acid	39.19	22	1.98
Protoxide of iron	47.96	36	1.33
„ manganese	9.50	35	0.27
Magnesia	3.12	20	0.15
	<u>99.77</u>		

Since $1.75 : 1.78 :: 1 : 1$, chalybite is a mixture of isomorphous carbonates consisting of one equivalent of the base and one equivalent of the acid, RO CO_2 , and since the equivalents of magnesia, protoxide of manganese and protoxide of iron are pretty nearly as $1 : 2 : 9$, the mixture would be

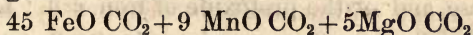
denoted by the formula:



which when computed gives:

12	equivalents of carbonic acid	=	264	=	38.94
9	„ protoxide of iron	=	324	=	47.79
2	„ „ manganese	=	70	=	10.32
1	„ of magnesia	=	20	=	2.95
			<u>678</u>		<u>100.00</u>

Observation.—According to the analysis the atomic relation of magnesia, the protoxide of iron and of manganese is properly as 15 : 27 : 133 = 5 : 9 : 45, and we should be obliged to regard the formula as:



numerically as:

59	equivalents of carbonic acid	=	1298	=	38.94
45	„ protoxide of iron	=	1620	=	48.69
9	„ „ manganese	=	315	=	9.45
5	„ magnesia	=	100	=	3.01
			<u>3333</u>		<u>100.00</u>

If the computation is compared, in accordance with both formulas, with the numbers found, the differences for the two formulas will be as follows:

	First formula.	Second formula.
Carbonic acid	— 0.25	— 0.25
Protoxide of iron	— 0.17	+ 0.64
Protoxide of manganese	— 0.82	+ 0.05
Magnesia	— 0.17	+ 0.11

Whilst the two formulas are almost equally valid for carbonic acid and magnesia, the second is less favorable for iron from the fact that it corresponds better with the quantity of manganese found. Therefore the second formula has no distinct advantage over the first; consequently here, as in all similar cases, the simpler ratio will be preferred.

The computation by means of the quantities of oxygen will furnish the following results, if

11 carbonic acid = 8 oxygen

9 protoxide of iron = 2 „

35 protoxide of manganese = 8 „

5 magnesia = 2 „

then

39.19 parts of carbonic acid contain 28.50 of oxygen.

47.96	„	protoxide of iron	„	10.66	} 14.08	
9.50	„	„	manganese	„		2.17
3.12	„	magnesia	„	1.25		

The oxygen of the bases and that of the acid = 1 : 2 ; the mixture consequently = RO CO_2 .

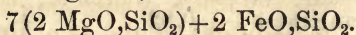
Furthermore the oxygen of the magnesia, of the protoxide of manganese and of the protoxide of iron = 1 : 1.7 : 8.5 = 1.2 : 2 : 10 = 1 : 1.8 : 9, or nearly = 1 : 2 : 9.

Olivine.—Olivine from meteorites, commonly called Pallas meteorite, contains according to Berzelius:

Chem : Eq : Quotients.

Silicic acid	40.86	30	1.36	} 2.70
Magnesia	47.35	20	3.37	
Protoxide of iron	11.72	36	0.33	
	<u>99.93</u>			

The equivalents of the acid and of the bases are as 1 : 2 ; olivine is therefore an isomorphous mixture of subsilicates, $2\text{RO}, \text{SiO}_2$, that is, since $0.33 : 2.37 :: 1 : 7$, of 1 equivalent of the silicate of the protoxide of iron and 7 equivalents of the silicate of magnesia, thus:



Computed numerically:

8 equivalents of silicic acid	=	240	=	40.54
14 „ „ magnesia	=	280	=	47.30
2 „ „ protoxide of iron	=	72	=	12.16
		<u>592</u>		<u>100.00</u>

The computation by means of the oxygen ratios is:

15 silicic acid = 8 oxygen

5 magnesia = 2 „

9 protoxide of iron = 2 „

Therefore we have the quantities of oxygen in

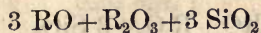
Silicic acid		21.79
Magnesia	18.94	} 21.54
Protoxide of iron	2.60	

They are consequently equal in the acid and the bases, so that the mixture is denoted by the formula $2 \text{RO}, \text{SiO}_2$; and since $2.60 : 18.94 = 1 : 7.3$, that is nearly $= 1 : 7$, the preceding formula is corroborated.

Garnet.—A variety of garnet from Sala is constituted according to Bredberg as follows:

	Chem: Eq: Quotients.			
Silicic acid	36.62	30	1.220	
Alumina	7.53	51.3	0.147	} 0.424
Protoxide of iron	22.18	80	0.277	
Lime	31.80	28	1.136	} 1.234
Magnesia	1.95	20	0.098	
	100.08			

The sum of the equivalents of the bases, and that of the acid have the ratio to each other of $1 : 1.36 = 3 : 4.08$. If we assume this ratio to be as $3 : 4$, it is evident that garnet is an isomorphous mixture containing three equivalents of silicic acid for every four equivalents of the bases. But the latter are different in their conditions, two of them, for instance alumina and the oxide of iron, being isomorphous as sesquioxides (R_2O_3), whilst lime and magnesia are isomorphous as protoxides (RO). The mixture, therefore, is constituted of isomorphous double silicates of the two kinds of bases. Since now the equivalents R_2O_3 and RO have the ratio of $0.424 : 1.234 = 1 : 3$, the mixture is a compound of 3 equivalents of RO , 1 of R_2O_3 and 3 of SiO_2 :

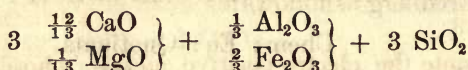


From the special formula we derive as follows: the equivalents of alumina and the sesquioxide of iron $= 0.147 : 0.277 = 1 : 1.9$, which we must assume as $1 : 2$. Those of magnesia and lime $= 0.098 : 1.136 = 1 : 11.6$, for which we as-

sume 1 : 12. According to this view $\frac{1}{3} R_2O_3 =$ alumina, $\frac{2}{3} =$ sesquioxide of iron; $\frac{1}{13}$ of 3 RO = magnesia, $\frac{12}{13} =$ lime, from which numerically we have the following:

3 equivalents of silicic acid	=	90	=	37.11
$\frac{1}{3}$ „ alumina	=	17.1	=	7.05
$\frac{2}{3}$ „ sesquioxide of iron	=	53.3	=	21.98
$\frac{36}{13}$ „ lime	=	77.5	=	31.96
$\frac{3}{13}$ „ magnesia	=	4.6	=	1.90
		242.5		100.00

The special formula would be:



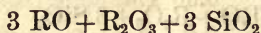
The following are used as a basis in the computation by means of the proportions of oxygen:

15 silicic acid	=	8	oxygen.
100 alumina	=	46.8	„
10 sesquioxide of iron	=	3	„
7 lime	=	2	„
4 magnesia	=	2	„

From which we receive the following proportionate quantities of oxygen:

36.62 silicic acid	=	19.53	
7.53 alumina	=	3.52	$\left. \begin{array}{l} 10.17 \\ 9.87 \end{array} \right\} 20.04$
22.18 sesquioxide of iron	=	6.65	
31.80 lime	=	9.09	
1.95 magnesia	=	0.78	

From this computation it follows, that the oxygen of the protoxides and of the sesquioxides has the ratio of 1 : 1, also that the oxygen of the bases together, and that of the acid have the same ratio of 1 : 1, which again leads to the same formula as before:



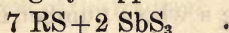
Furthermore $3.52 : 6.65 = 1 : 1.9$ and $0.78 : 9.09 = 1 : 11.6$ for which we may substitute 1 : 2 and 1 : 12.

Grey Copper.—In a variety of this mineral from Wolfach H. Rose found the following:

		Chem: Eq:	Quotients.
Sulphur	23.52	16	1.147
Antimony	26.63	120.3	0.221
Copper	25.23	63.4*	0.398
Silver	17.71	108	0.164
Iron	3.72	28	0.133
Zinc	3.10	32.5	0.095
	<u>99.91</u>		

The sum of the equivalents of all the metals, and that of the sulphur have the ratio to each other of $1.011 : 1.47 = 1 : 1.45 = 9 : 13$.

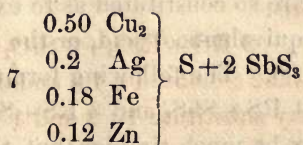
If we denote the electro-positive metals, whose sulphides contain 1 equivalent of sulphur, with R, the equivalents of antimony and R will stand in the ratio of $0.22 : 0.79 = 2 : 7$, or those of antimony, R and sulphur will have the ratio of $2 : 7 : 13$; and since 7 equivalents of antimony require 6 of sulphur, the formula for grey copper would be:



The chemical equivalents of Zn : Fe : Ag : Cu₂ furthermore have the ratio to each other as $1 : 1.4 : 1.7 : 4.2$. Let us assume for them the following ratio of $1 : 1\frac{1}{2} : 1\frac{2}{3} : 4\frac{1}{3} = 6 : 9 : 10 : 25$, and then compute them numerically:

13 equivalents of sulphur	=	208.0	=	23.52
2 „ antimony	=	240.6	=	27.20
$7 \times \frac{25}{6} = \frac{7}{2}$ „ copper	=	221.9	=	25.09
$7 \times \frac{10}{6} = \frac{7}{3}$ „ silver	=	151.2	=	17.10
$7 \times \frac{9}{6} = \frac{63}{6}$ „ iron	=	35.3	=	4.00
$7 \times \frac{6}{6} = \frac{21}{6}$ „ zinc	=	27.3	=	3.09
		<u>884.3</u>		<u>100.00</u>

The special formula would have to be written:



*Since the sulphide of copper, Cu₂S, in this and similar minerals is isomorphous with the remaining RS, 2 equivalents of copper must be employed in the calculation.

The second mode of computation assumes the following data :

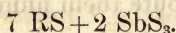
71.5	antimony	=	100	sulphide of antimony, SbS_3 .
79.86	copper	=	100	sulphide of copper, Cu_2S .
87.1	silver	=	100	sulphide of silver, AgS .
7	iron	=	11	sulphide of iron, FeS .
67	zinc	=	100	sulphide of zinc, ZnS .

These require therefore :

26.63	antimony	=		10.62	sulphur
25.23	copper	=	6.36	} 12.64	,,
17.71	silver	=	2.62		
3.72	iron	=	2.13		
3.10	zinc	=	1.53		
				<hr/>	23.26 sulphur

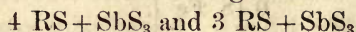
Now since 23.52 parts of sulphur were found, the difference is + 0.26 per cent.

The numbers 12.64 and 10.62 must stand in a simple ratio to each other having a whole number for the first, when the latter = 3, or a multiple of this number (since 1 equivalent of sulphide of antimony contains 3 equivalents of sulphur). They have the ratio of $3.5 : 3 = 7 : 6$, that is, grey copper is represented by the formula :



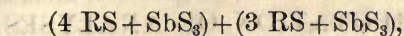
Furthermore the quantities of zinc, iron, silver and copper have the ratio of $1 : 1.4 : 1.7 : 4.1$, as was found before.

If we examine more intimately the results of the analysis that have been here submitted to computation, it will be observed, that these results do not furnish quite simple ratios of composition, as we ought to expect. For the separate isomorphous sulphur salts, which enter into the formation of grey copper, are so constituted as to exhibit 7 equivalents of base with 2 equivalents of acid, or the amounts of sulphur in the two as $7 : 6$. The following formulas :

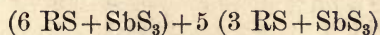


would undoubtedly be much simpler, but they do not correspond with the results of the analysis. For although the

accurate analysis of a specimen of grey copper is fraught with many difficulties, the name of the author of the analysis in question is sufficient guarantee against any very serious error, and the only question, that might possibly arise, would be whether the far from simple ratio of $7 \text{ RS} + 2 \text{ SbS}_3$ might not be regarded as



or,



that is, whether each separate member of the grey copper mixture might not be looked upon as a double salt, which would furnish very simple ratios between the base and the acid in the latter case (2 : 1 and 1 : 1). But this would be mere hypothesis.

Cases like this in the analysis of minerals are not rare. A *single* analysis, even when it is quite accurate, leaves a doubt as to the true composition of the mineral, because of the possibility that the mineral was not quite pure, fresh and unchanged. It is thus absolutely necessary to make a number of analyses of the varied specimens of a mineral as found in different localities, and to compare the results with one another. This leads to the theory of the *Constitution* of chemical compounds, the determination of their *atomic weights* and their *rational formulas*, a branch of chemistry not comprehended in the aim of the present work, but belonging to the province of general theoretic chemistry.

TABLES

for the

COMPUTATION OF ANALYSES.

	Chem: Eq:	
ALUMINIUM	Al=13.65	
Alumina	$\text{Al}_2\text{O}_3=51.3$	46.8 pCt of oxygen
ANTIMONY	Sb=120.3	
Antimonious acid	$2 \text{ SbO}_4=304.6$	79.0 „ antimony
Sulphide of antimony	$\text{SbO}_3=168.3$	71.5 „ antimony 28.5 „ sulphur
ARSENIC	As=75	
Arsenious acid	$\text{AsO}_5=115$	34.78 „ oxygen
Arsenate of ammonia	$2 \text{ MgO}, \text{AsO}_5 +$	60.53 „ arsenic acid
and magnesia	$\text{NH}_3 + 2 \text{ aq } 190$	39.47 „ arsenic
Sulphide of arsenic	$\text{AsS}_3=123$	60.98 „ arsenic 39.02 „ sulphur
BARIUM	Ba=68.55	
Baryta	$\text{BaO}=76.55$	10.45 „ oxygen
Sulphate of baryta	$\text{BaSO}_4=116.55$	65.68 „ baryta
Silico-fluoride of barium	$\text{BaFl} + \text{SiFl}_2$ $=139.55$	54.85 „ baryta
BORON	B=11	
Boracic acid	$\text{BO}_3=35$	68.57 „ oxygen
Boro-fluoride of potas ^m	$\text{KFl} + \text{BFl } 126$	27.78 „ boracic acid
BROMINE	Br=80	
Bromide of silver	$\text{AgBr}=198$	41.55 „ oxygen
Cæsium	Cs=123.3	
Oxide of cæsium	$\text{CsO}=131.3$	6.09 „ oxygen
CALCIUM	Ca=20	
Lime	$\text{CaO}=28$	28.57 „ oxygen

	Chem : Eq :	per cent
Carbonate of lime	$\text{CaO}, \text{CO}_2 = 50$	56 „ of lime
Sulphate of lime	$\text{CaO}, \text{SO}_3 = 68$	41.18 „ lime (7 lime = 2 oxygen)
BISMUTH	$\text{Bi} = 104$	
Oxide of bismuth	$\text{Bi}_2\text{O}_3 = 232$	10.34 „ oxygen
Basic chloride of bismuth	$\text{Bi}_2\text{Cl}_3 + 2\text{Bi}_2\text{O}_3 = 778.5$	6.16 „ oxygen 80.15 „ bismuth 89.4 „ oxide of do
CADMIUM	$\text{Cd} = 56$	
Oxide of cadmium	$\text{CdO} = 64$	12.5 „ oxygen (8 oxide of cadmium = 1 oxygen)
Sulphide of cadmium	$\text{CdS} = 72$	22.2 „ sulphur (9 sulphide of cadmium = 2 sulphur)
CARBON	$\text{C} = 6$	
Carbonic acid	$\text{CO}_2 = 22$	72.72 „ oxygen (11 carbonic acid = 8 oxygen)
Oxalic acid	$\text{C}_2\text{O}_3 = 36$	66.66 „ oxygen (3 oxalic acid = 2 ox ⁿ)
Carbonate of lime	$\text{CaO}, \text{CO}_2 = 50$	44 „ carbonic acid
CERIUM	$\text{Ce} = 46$	
Oxide of cerium	$\text{CeO} = 54$	14.8 „ oxygen
CHLORINE	$\text{Cl} = 35.5$	
Chloride of silver	$\text{AgCl} = 143.5$	24.74 „ chlorine
CHROMIUM	$\text{Cr} = 26$	
Oxide of chromium	$\text{Cr}_2\text{O}_3 = 76$	31.58 „ oxygen 131.6 „ chromic acid
Chromic acid	$\text{CrO}_3 = 50$	48 „ oxygen
Chromate of the oxide of lead	$\text{PbO}, \text{CrO}_3 = 161.5$	30.96 „ chromic acid 23.53 „ chrome
COBALT	$\text{Co} = 30$	
Oxide of cobalt	$\text{CoO} = 38$	21.05 „ oxygen
COPPER	$\text{Cu} = 31.7$	
Suboxide of copper	$\text{Cu}_2\text{O} = 71.4$	11.2 „ oxygen
Oxide of copper	$\text{CuO} = 39.7$	20.14 „ oxygen
Subsulphide of copper	$\text{Cu}_2\text{S} = 79.4$	79.86 „ copper

	Chem: Eq:	per cent
Subsulphide of copper		20.14 „ sulphur 100. „ oxide of copper
Didymium	Di=48	
Oxide of didymium	DiO=56	14.28 „ oxygen (7 ox ^e of did ^m =1 oxy ⁿ)
Fluorine	Fl=19	
Fluoride of calcium	CaFl=39	48.72 „ fluorine
Glucinum	G=7	
Oxide of glucinum	G ₂ O ₃ =38	63.19 „ oxygen
Gold	Au=196	
Hydrogen	H=1	
Water	HO=9	88.89 „ oxygen (9 water=8 oxygen)
Ammonia	NH ₃ =17	32.35 „ nitrogen 153 „ oxide of ammonium
Oxide of ammonium	AmO=26	30.77 „ oxygen
Chloride of ammonium	AmCl=53.5	26.17 „ nitrogen 31.77 „ ammonia 48.6 „ oxide of ammonium
Iodine	I=127	
Iodide of silver	AgI=235	54.04 „ iodine
Iodide of palladium	PdI=180	70.55 „ „
Iridium	Ir=99(?)	
Iron	Fe=28	
Protoxide of iron	FeO=36	(9 protoxide of iron = 2 oxygen)
Sesquioxide of iron	Fe ₂ O ₃ =80	30 „ oxygen (sesquioxide of iron = 3 oxygen) 90 „ protoxide of iron (10 sesquioxide of iron = 9 protoxide)
Sulphide of iron	FeS=44	36.36 „ sulphur (11 sulphide of iron = 4 of sulphur)
Lanthanum	La=46.5-47 (?)	
Lead	Pb=103.5	

	Chem: Eq:	per cent
Oxide of lead	$\text{PbO}=111.5$	7.175 „ oxygen
Sulphide of lead	$\text{PbS}=119.5$	86.6 „ lead
		13.4 „ sulphur
Sulphate of the oxide of lead	$\text{PbO}, \text{SO}_3=151.5$	73.6 „ oxide of lead
		68.32 „ lead
Chloride of lead	$\text{PbCl}=139$	74.46 „ lead
LITHIUM	$\text{Li}=7$	
Lithia	$\text{LiO}=15$	53.33 „ oxygen
		(15 lithia=8 oxygen)
Chloride of lithium	$\text{LiCl}=42.5$	35.29 „ lithia
MAGNESIUM	$\text{Mg}=12$	
Magnesia	$\text{MgO}=20$	40 „ oxygen
		(5 magnesia=2 oxy ⁿ)
Pyrophosphate of magnesia	$\text{Mg}_3\text{OP}, \text{O}_5=111$	36.03 „ magnesia
MANGANESE	$\text{Mn}=27$	
Protoxide of manganese	$\text{MnO}=35$	22.86 „ oxygen
Sesquioxide of do	$\text{Mn}_2\text{O}_3=78$	30.77 „ do
Hausmannite	$\text{MnOMn}_2\text{O}_3=113$	71.68 „ manganese
		92.92 „ protoxide of manganese
		103.54 „ sesquioxide of manganese
Binoxide of manganese	$\text{MnO}_2=43$	62.8 „ manganese
MERCURY	$\text{Hg}=100$	
Oxide of mercury	$\text{HgO}=108$	7.4 „ oxygen
Sulphide of mercury	$\text{HgS}=116$	86.2 „ mercury
		13.8 „ sulphur
Chloride of mercury	$\text{Hg}_2\text{Cl}=235.5$	84.92 „ mercury
MOLYBDENUM	$\text{Mo}=46$	
Molybdic acid	$\text{MoO}_3=70$	34.28 „ oxygen
NICKEL	$\text{Ni}=29$	
Oxide of nickel	$\text{NiO}=37$	31.62 „ do
NIOBIUM	$\text{Nb}=49 (?)$	
Nitrogen	$\text{N}=14$	
Nitric acid	$\text{NO}_5=54$	74.07 „ do
OSMIUM	$\text{Os}=100 (?)$	
OXYGEN	$\text{O}=8$	

	Chem: Eq:	per cent
PALLADIUM	Pd=53	
PHOSPHORUS	P=31	
Phosphoric acid	PO ₅ =71	56.34 „ oxygen
Pyrophosphate of magnesia	Mg ₂ O, PO ₅ = 111	63.97 „ phosphoric acid
Phosphate of lime	3CaO, PO ₅ =155	45.80 „ do
PLATINUM	Pt=99	
Potassio-chloride of platinum	KCl+PtCl ₂ = 244.5	40.49 „ platinum
Ammonio-chloride of platinum	AmCl+PtCl ₂ =223.5	6.26 „ nitrogen 7.6 „ ammonia 11.63 „ oxide of am- monium
For 100 of platinum		14.14 „ nitrogen 17.17 „ ammonia 26.26 „ oxide of am- monium
POTASSIUM	K=39	
Potassa	KO=47	17 „ oxygen
Chloride of potassium	KCl=74.5	52.35 „ potassium 63.1 „ potassa
Sulphate of potassa	KO, SO ₃ =87	54 „ potassa
Potassio-chloride of platinum	KCl+PtCl ₂ = 244.5	19.22 „ potassa 30.47 „ chloride of potassium
RHODIUM	Rh=52	
RUBIDIUM	Rb=85.36	
Rubidia	RbO=93.36	8.57 „ oxygen
RUTHENIUM	Ru=52 (?)	
SELENIUM	Se=39.5	
SILVER	Ag=108	
Oxide of silver	AgO=116	6.9 „ do
SODIUM	Na=23	
Soda	NaO=31	25.8 „ do
Chloride of sodium	NaCl=58.	39.32 „ sodium 53 „ soda
Sulphate of soda	NaOSO ₃ =71	43.66 „ soda
STRONTIUM	Sr=44	
Strontia	SrO=52	5.4 „ oxygen

	Chem : Eq :	per cent
Sulphate of strontia	$\text{SrOSO}_3 = 92$	56.52 „ strontia
SULPHUR	$\text{S} = 16$	
Sulphuric acid	$\text{SO}_3 = 40$	60 „ oxygen (5 sulphuric acid = 3 oxygen)
Sulphate of baryta	$\text{BaO}, \text{SO}_3 = 116.55$	34.32 „ sulphuric acid 13.73 „ sulphur
TANTALUM	$\text{Ta} = (?)$	
TELLURIUM	$\text{Te} = 64$	
THALLIUM	$(?)$	
THORIUM	$\text{Th} = 59.16$	
TIN	$\text{Sn} = 58.8$	
Stannic acid	$\text{SnO}_3 = 74.8$	21.4 „ oxygen
TITANIUM	$\text{Ti} = 24$	
Titanic acid	$\text{TiO}_2 = 40$	40 „ do (5 titanic acid = 2 oxygen)
TUNGSTEN	$\text{W} = 92$	
Tungstic acid	$\text{WO}_3 = 116$	20.7 „ oxygen
URANIUM	$\text{U} = 60$	
VANADIUM	$\text{V} = 68.5$	
YTTRIUM	$\text{Y} = 35(?)$	
ZINC	$\text{Zn} = 32.5$	
Oxide of zinc	$\text{ZnO} = 40.5$	19.75 „ do
Sulphide of zinc	$\text{ZnS} = 48.5$	33 „ sulphur
ZIRCONIUM	$\text{Zr} = 45$	
Zirconic acid	$\text{ZrO}_2 = 61$	26.23 „ oxygen

INDEX

A.

Acidimetry, 42.
 Alkalimetry, 42.
 Alloys, 47.
 Alum, 113.
 Alumina, 113.
 Ammonia, 113.
 Analcime, 152.
 Analysis by measure, 40.
 Analysis by weight, 71.
 Antimony, 61.
 Apatite, 117.
 Argentan, 54.
 Arsenic, 92.
 Axinite, 163.

B.

Basalt, 186.
 Baryta, 111.
 Bell metal, 57.
 Berthierite, 86.
 Bismuth, 55.
 Bitterspar, 131.
 Black oxide of manganese, 69.
 Black vitriol, 115.
 Blende, 85.
 Block tin, 59.
 Blue iron ore, 122.
 Bog iron ore, 65.
 Bone black, 119.
 Boracic acid, 137.
 Borates, 135.
 Boronatrocalcite, 137.
 Boulangerite, 91.
 Bournonite, 92.

Brass, 51.

Brittle silver ore, 91.

Bronze, 57.

Brown hematite, 65.

Brown lead ore, 121.

Bunsen's analysis, 71.

C.

Cadmium, 60.

Calamine, 159.

Cannon metal, 57.

Carbonates, 128.

Celestine, 111.

Chabasite, 152.

Childrenite, 127.

Chlorides, 93.

„ of ammonium, 174.

„ of calcium, 117.

„ of lead, 121.

Chromates, 193.

Chrome iron ore, 192.

„ orange, red, yellow, 193.

„ mica, 163.

„ ochre, 162.

Chrysoberyl, 162.

Chrysoprase, 162.

Clay, 65.

Cobalt glance, 99.

Compounds of fluorine, 198.

„ of titanium, 196.

Computation of analyses, 202.

Construction of formulas, 199.

Copper, 49, &c.

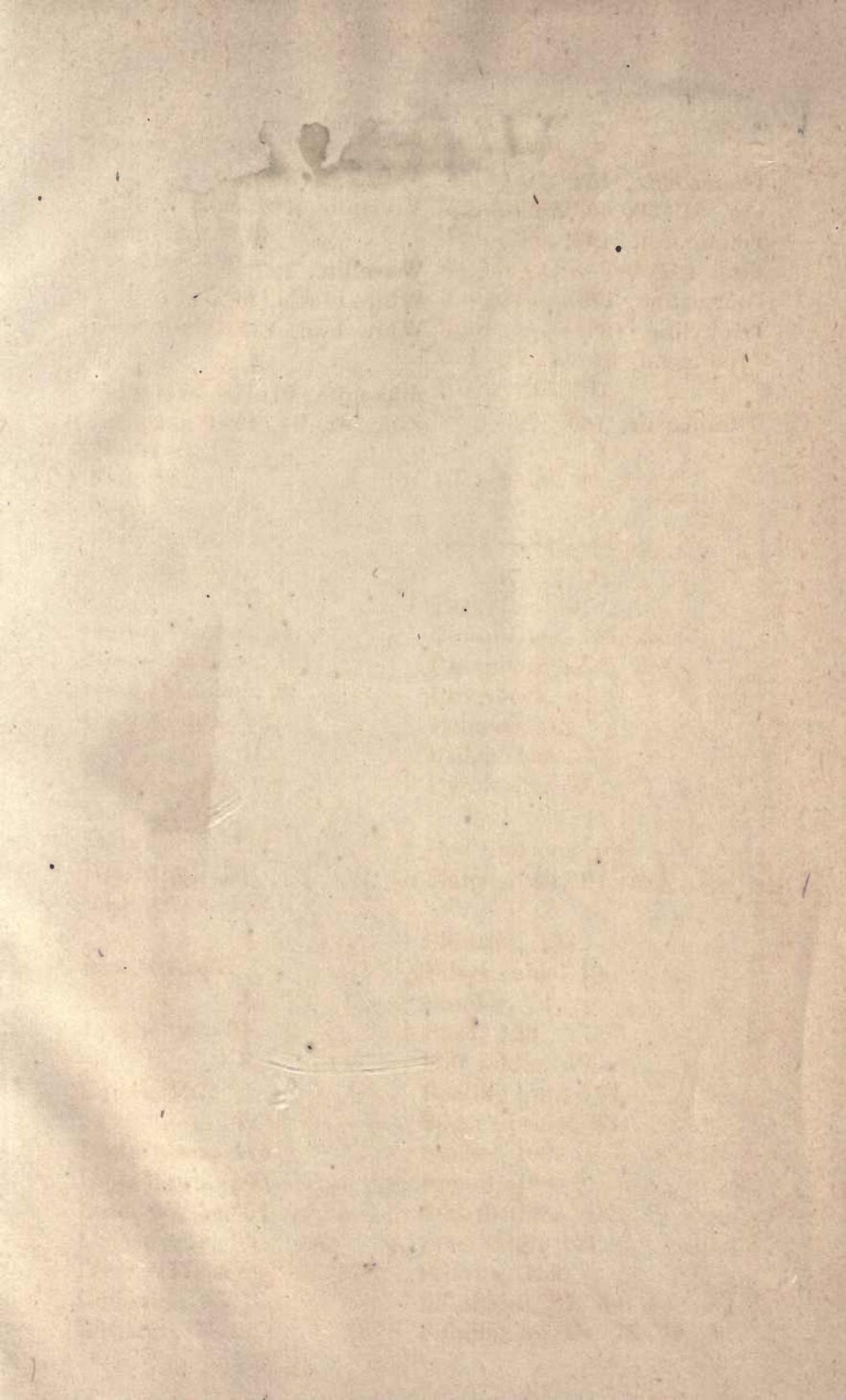
„ glance, 83.

„ nickel, 99.

- Copper pyrites, 83.
 ,, slags, 158.
 ,, stone, 95.
 Corundum, 190.
 Cryolite, 199.
 D.
 Dolomite, 131.
 F.
 False gold leaf, 51.
 Feather ore, 91.
 Fluorine, 170.
 Foil, 59.
 Forge slags, 68.
 Franklinite, 190.
 Fusible alloys, 59.
 G.
 German silver, 54.
 Green lead ore, 121.
 Grey antimony, 86.
 Grey copper, 92.
 H.
 Hausmannite, 69.
 Haüyne, 160.
 Heavy spar, 110.
 Hematite, 65.
 Heulandite, 152.
 I.
 Iron, 64, &c.
 J.
 Jamesonite, 91.
 K.
 Kalait, 127.
 L.
 Lamp black, 119.
 Lapis lazuli, 160.
 Lead, 55, 56, 57, 59, &c.
 Leucopyrite, 95.
 Lime, 111, &c.
 Limonite, 65.
 Litharge, 75.
 Lithia, 123.
 M.
 Magnesia, 131, &c.
 Magnetite, 83.
 Magnoferrite, 190.
 Manganese, 69.
 Mesotype, 152.
 Mercury, 61.
 Miargyrite, 91.
 Mispickel, 98.
 N.
 Nickel, 54, 99, 103.
 O.
 Oxides, 64, of lead, 75.
 P.
 Packfong, 54.
 Phosphates, 116, &c.
 Phosphoric acid, 126.
 Pinchbeck, 51.
 Potassa, 113.
 Psilomelane, 73.
 Pyrolusite, 69.
 R.
 Red lead ore, 193.
 Ruby silver, 91, 209.
 S.
 Silicates, 138.
 Silver coins, 49.
 Similor, 51.
 Soda, 123.
 Soft solder, 59.
 Spathic iron, 134.
 Spear pyrites, 83.
 Speise, 103.
 Spinel, 190.
 Stassfurthite, 138.
 Steel slags, 151.
 Stilbite, 152.
 Sulphides, 87, &c.
 Sulphur metals, 78, 79, &c.

S.	V.
Thomsonite, 152.	Vitriol, 115.
Tin, 57, 59, 60, &c.	Vivianite, 122;
Titanic iron, 196.	W.
Tiza, 137.	Wavellite, 127.
Tourmaline, 173.	White nickel, 99.
Triphyline, 123.	White lead, 135.
Type metal, 61.	Z.
U.	Zinkenite, 91.
Ultramarine, 160.	Zinc, 92, 94, 159.





THIS BOOK IS DUE ON THE LAST DATE
STAMPED BELOW

AN INITIAL FINE OF 25 CENTS
WILL BE ASSESSED FOR FAILURE TO RETURN
THIS BOOK ON THE DATE DUE. THE PENALTY
WILL INCREASE TO 50 CENTS ON THE FOURTH
DAY AND TO \$1.00 ON THE SEVENTH DAY
OVERDUE.

JUN 29 1938

JUN 28 2003

AUG 6 1940

5 May '58 CB
APR 22 1953 LU

22 May '53 PW

MAY 8 1953 LU

20 Jul '62 RC

REC'D LD

JUL 6 1962

LD 21-95m-7,'37

QD101

R3Z

44272

